MgO REMOVAL FROM PHOSPHATE PEBBLE BY FLOTATION

Prepared by

The University of Florida

under a grant sponsored by

FIPR

Florida Institute of Phosphate Research

April 2003

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MgO REMOVAL FROM PHOSPHATE PEBBLE
BY FLOTATION

FINAL REPORT

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April 2003

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PERSPECTIVE

Patrick Zhang, Research Director - Beneficiation & Mining

With the depletion of the higher grade, easy-to-process Bone Valley deposits, the central Florida phosphate industry has moved into the lower grade, more contaminated ore bodies from the Southern Extension. The phosphate deposits in the Southern Extension may be divided into two zones, an upper zone and a lower zone. The upper zone is readily upgradeable using the current technology, but the lower zone is highly contaminated by dolomite. A majority of the dolomite in the lower zone is concentrated in the pebble (plus 1 mm) fraction.

In 1994, FIPR conducted a comparative evaluation on five seemingly promising flotation processes for separating dolomite from dolomitic phosphate pebbles, utilizing the same flotation feed. Two of the processes failed to produce a concentrate of less than 1% MgO, and all the processes gave very poor overall phosphate recovery ranging from 30-60%.

Perhaps the most promising process for Florida dolomitic phosphate pebbles is the CLDRI (Chinese Lianyungang Design and Research Institute) process developed under FIPR funding. In this process, dolomitic pebbles are ground to suitable particle sizes (normally to -100 mesh) for liberating dolomite and other impurities from phosphate. The ground flotation feed is first subject to dolomite flotation using a proprietary fatty acid soap as the dolomite collector under slightly acidic pH adjusted with a mixture of H_3PO_4 and H_2SO_4. The sink product of dolomite flotation is further upgraded by either silica or phosphate flotation. A recently completed pilot-testing program demonstrated both the technical and economic feasibility of the CLDRI process for Florida dolomitic pebbles.

However, like most flotation processes for the high-dolomite pebble, the CLDRI process requires fine grinding. Fine grinding is energy intensive, and comes with some materials handling challenges. It is therefore of great interest to separate dolomite from phosphate with as little grinding as possible. The current project, conducted by University of Florida, showed the possibility of achieving that separation without any grinding. This novel process involves coating the pebble with a surfactant, attacking the coated pebble with a dilute sulfuric acid, and removing the dolomite particles lifted by CO_2 bubbles. The CO_2 bubbles are generated by the reaction of dolomite with sulfuric acid.

The encouraging results presented in this report were all derived from small-scale batch tests. Many challenges remain in scaling up this process, such as the method of coating the particles, design of the separator, speed of the reaction, and control of the acid strength and saturation.

ABSTRACT

Phosphate rock as it is mined in Florida contains an increasing quantity of magnesium. The magnesium is present as discrete particles of dolomite (calcium magnesium carbonate) and generally in particles of rock larger than 1 mm. The higher magnesium both adversely affects the production of phosphoric acid (lowers phosphate recovery or rate) and acts as a diluent in the final fertilizer products.

Numerous surfactants and surfactant systems were used to coat mixtures of dolomite and phosphate rock. The coated rock (sizes up to 10 mm) was then immersed in a weak (2-3%) sulfuric solution. The acid reacted with the dolomite, generating carbon dioxide that could be trapped by the surfactant and cause the dolomite to float to the surface. Of the surfactant/surfactant systems tried, polyvinyl alcohol (PVA) was found to be the best performer. This surfactant could float particles up to 8 mm in size.

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EXECUTIVE SUMMARY

Separation of dolomitic limestone impurities from apatite has become increasingly important, especially with the depletion of current high-grade phosphate deposits. Phosphoric acid production from phosphate rock dictates that the phosphate feed to the chemical plants contain no more than 1% MgO, and generally the MgO must be below 0.6% to produce on-grade DAP.

The presence of higher MgO content is reported to increase the viscosity of the phosphoric acid, resulting in higher pumping cost, lower filtration rates, increased phosphate losses, and reduced nutrient concentration in fertilizer products. Since the MgO source is mostly dolomite (a mixture of calcium and magnesium carbonate), it also increases the gypsum generation rate per ton of P_2O_5.

Most of the MgO exists as liberated dolomite particles and is amenable to removal by physical separation processes. Several attempts in the past have been made to remove dolomite from apatite, however none of these processes produces a phosphate concentrate less than 1% MgO on a commercial scale.

While there are several processes under investigation that do a better job of removing the magnesium, they require grinding of the pebble-size rock (which contains the bulk of the dolomite) to a fine degree and generally require several unit operations.

It is well known that the dolomite particles generate CO_2 when exposed to acid solution. If the generated CO_2 is contained around the particle by the use of a good surfactant or coating agent, then the dolomite will be selectively floated and separated from the phosphate rock. While this may not be possible with large size pebbles, it should work with the smaller sized pebble and the crushed (not ground) oversize pebble.

The major objective of this project was to conduct a bench-scale investigation to develop a new process for the removal of MgO from phosphate pebble without grinding the pebble. The new methodology separates the dolomite from phosphate pebble by flotation through the use of a surfactant to capture the gas generated by the reaction of the dolomite with acid. This investigation is summarized as:

- Test different types of surfactants (anionic, cationic, nonionic, and polymers)
- Test different acid types (sulfuric, nitric, HCl, and acetic acid)
- Test different acid concentrations
- Establish a procedure for such flotation tests
- Determine the particle size suitable for flotation
- Investigate the effect of operating variables
- Test the flotation of dolomite using pond water
- Test the flotation of dolomite under dynamic conditions

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In this study, preliminary tests were conducted to test different surfactant types and dosages, different acid types and concentrations, and different particle sizes. Initial tests were conducted in beakers using discrete dolomite particles dipped or coated with a surfactant or surfactant system. Observations were then made as to the rate and adherence of generated gas to the particles, the time required to float the particle to the surface and the long-term stability of the floated particles.

In the initial screening tests, conducted with a variety of surfactants, it was observed that the performance of anionic surfactants was better than that of nonionic surfactants, which in turn were better than cationic surfactants which were essentially ineffective. However, even the best performing anionic surfactants could not float particles above 4 mm in size or keep the floated particles at the surface for more than a few minutes.

After additional tests with a wide variety of coating agents and coating systems, polyvinyl alcohol was found to be the most effective. While it did require a higher acid concentration (3% sulfuric) to work effectively, it could float particles up to 8 mm in size and maintain the floated particles at the surface for very long periods of time.

Tests were also conducted with various screen fractions of a high MgO pebble rock. The batch tests were conducted in a five-gallon bucket and the floated material removed from the top of the bucket after time periods up to 24 hours. The floated fractions contained 11-16% MgO and 3-5% P_2O_5; the fraction that did not float contained less than 1.5% MgO and over 20% P_2O_5. While these tests did demonstrate efficient separation, the non-floating fraction contained a lower quantity of phosphate than expected. Further analytical tests were conducted with the non-floated rock that had been in contact with the 3% sulfuric acid for 24 hours and it was found that it contained a significant quantity of gypsum. After correcting for the dilution effect of the gypsum, the non-floated rock contained 62-65 BPL, which is consistent with rock containing 1.2-1.7% MgO.

INTRODUCTION

As phosphate mining operations continue to move southward in central Florida, there is an increase in the MgO content of the rock. This MgO increases the difficulty in processing the rock (lowers the P_2O_5 recovery) and makes it difficult to make DAP grade. In fact, much of the higher MgO rock is simply left in the ground, as there is no economical method for removing it from the rock. At present, the only method ever commercialized, heavy media separation, is sitting idle due at least partially to its relatively high operating cost and poor performance. The heavy media product typically contains 1% or above MgO and less than half the BPL tons. The high MgO rock is now either discarded or blended off with lower MgO rock. The separation efficiency (P_2O_5 recovery in the sink + MgO recovery in the float)/2 is estimated to be in the 55-70% range.

Over the years, FIPR and the industry have looked at a number of methods for removal of the MgO. They include selective flotation, flocculation, grinding and screening, and partial acidification (El-Shall 1994; Hanna and Anazia 1990; Jacobs Engineering 1995; Laird and Hanson 1997). All flotation methods required that the rock be first ground to concentrate-size material or smaller prior to the flotation. While some of these have shown promise in the laboratory, none has been commercialized to date, generally due to either a complex flowsheet, poor economics or low BPL recovery. The most promising process evaluated to date is the CLDRI process. Its separation efficiency is 75-80%.

In general, when high MgO is encountered in the phosphate matrix, most of it is contained in the pebble fraction and the -150 mesh fraction (Smith and others 1997). The concentrate fraction typically contains less than 1% MgO, even if the pebble contains over 5% MgO. In addition, the MgO is contained mostly in granules of dolomite. Very little of the MgO is contained in the particles of apatite rock.

In fact, the particles of dolomite and apatite rock can be separated by hand, simply based on the color and texture of the particles. From a presentation made at the 1997 Regional Phosphate Conference (Stana 1997), the data in Tables 1 and 2 are presented.

Table 1. First Example of Rock Quality from Hand Separation.

	Initial Rock	Rock Fraction	Dolomite Fraction	% in Rock
BPL	55.65	66.92	49.16	49.8
Al_2O_3	0.69	0.70	0.68	42.9
Fe_2O_3	0.67	0.51	0.78	32.3
MgO	4.05	0.46	6.67	4.8
CaO/P_2O_5	1.80	1.49	2.03	
Wt %		37.7	62.3	

Table 2. Second Example of Rock Quality from Hand Separation.

	Initial Rock	Rock Fraction	Dolomitic Fraction	% in Rock
BPL	50.15	68.91	36.46	58.0
Al_2O_3	0.91	0.82	0.98	37.9
Fe_2O_3	0.93	0.59	1.17	26.9
MgO	5.06	0.52	8.37	4.3
CaO/P_2O_5	1.95	1.49	2.28	
Wt%		33.9	66.1	

This clearly demonstrates that it is possible to physically separate the high-MgO rock into a fraction that contains an acceptable quantity of MgO and as much as half the BPL tons of the initial rock.

METHODS AND TECHNIQUES

INTRODUCTION

A 100-pound sample of high dolomitic phosphate oversize pebble was obtained from the IMC Four Corners mine. This is not "normal" high-MgO rock, but the oversized high-MgO rock that is removed from pebble. As such neither the screen weight fractions nor the chemical analyses are representative of pebble. However, the rock is representative of the high dolomitic rock that needs to be separated.

SAMPLE PREPARATION

As-received material was first dried at 65° C. In cases where size reduction was required, the material was crushed and pulverized in a Bico pulverizer, and screened into the desired size range.

CHEMICAL ANALYSIS

Chemical analyses were performed using wet chemical methods, and the acid attack (digestion) method as described below.

About 0.5 gm of the dried and ground representative sample was digested in 50 ml of aqua regia by boiling 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, and the concentrations were measured using an Inductively Coupled Plasma (ICP) emission spectrometer.

Insoluble Analysis

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 allowing the crucible to cool, the acid insoluble in the sample was calculated.

Dolomite Flotation

Preliminary tests were conducted using different acid types (sulfuric, hydrochloric, nitric, acetic) within a concentration range (0.5-4% v/v), different types of surfactants (anionic, cationic, and nonionic), which were prepared as a 1-2% surfactant solution and used in two different ways: (1) surfactant was added to the acidic solution and/or (2) surfactant was used to coat the particles before adding the particles to the acidic solution.   Also, Mr. Bubbles® solution, latex paint, rubber cement, and polyvinyl alcohol (PVA) were used in this study. Vegetable and corn oil were used at the acidic solution/air interface and the oil height was 0.5-0.6 cm.

RESULTS AND DISCUSSION

DEVELOPMENT OF A LIST OF POTENTIAL SURFACTANTS FOR LAB TESTING

A list of potential surfactants was developed from a number of sources. Initially, a list was built from those available at the ERC. This was supplemented by those generated in a meeting on July 17, 2001. Faculty and students of the ERC, as well as Paul Clifford of FIPR, attended this meeting. Finally, additions were made to the list based on test observations and further inputs from attendees of the July 17th meeting. The total list is given in Table 3.

Table 3. List of Surfactants Tested.

Surfactant	Chemical Name (If Known)	Type (If Known)
Arquad® 12-50	Dodecanaminium+isopropyl alcohol	Cationic
Lilamine	N-3-aminopropyl-N-tallow alkyltrimethylenedi-	Cationic
Armac® HT	Amines, hydrogenated tallow alkyl acetates	Cationic
Armid® HT	Amides	Cationic
Armeen® 12 D	Dodecanamine	Cationic
Ethofat®	Tall oil	Anionic
SDSO$_3$	Sodium dodecyl-sulphonate	Anionic
SDSO$_4$	Sodium dodecyl-sulphate	Anionic
Oleic acid	Oleic acid	Anionic
Arlacel®	Sorbitan sesquioleate	Nonionic
Span®-20	Sorbitan monolautrate	Nonionic
G-1096	Polyoxyethelene-sorbitol hexaoleate	Nonionic
Brij-97	Polyoxyethelene oleyl ether	Nonionic
Arlatone™ T	Polyoxyethelene polyofatty acid ester	Nonionic
Tween®-21	Polyoxyethelene Sorbitan monolautrate	Nonionic
Tween®-85	Trioleate	Nonionic
Mr. Bubbles®	Lauryl succinate and mixed surfactants	
Latex paint		
PVA	Polyvinyl alcohol	
Rubber cement		

Note: Arquad, Armac, Armid, and Armeen, are registered trademarks of Akzona Incorporated Corporation. Arlacel, Arlatone, Brij, Span, and Tween are registered trademarks of ICI Americas, Inc; Ethofat is a registered trademark of Akzo Nobel Chemicals B.V. Corporation. Mr. Bubbles is a registered trademark of the Stromberger Corporation. Lilamin is a registered trademark of Kenobel Aktiebolag Corporation.

Initial Screening Tests

A 100-pound sample of high-dolomitic phosphate oversize pebble was obtained from the IMC Four Corners mine. This is not "normal" high-MgO rock, but the oversized high-MgO rock that is removed from pebble. As such, neither the screen weight fractions nor the chemical analyses are representative of pebble. However, the rock is representative of the high-dolomitic rock that needs to be separated. The rock was screened, with the results shown in Table 4.

Table 4. Size Analysis of a Representative Sample of High-MgO Pebble.

Size	Size, mm	Wt. %	% Cumulative (Passed)	% Cumulative (Retained)
+3/8 in	+9.5	11.62	100	11.62
-3/8 in +3.5 Mesh	-9.5+5.6	65.36	88.38	76.98
-3.5+6 Mesh	-5.6+3.36	18.14	23.02	95.12
-6+9 M	-3.36+2	2.05	4.88	97.17
-9+16 M	-2+1	1.6	2.83	98.77
-16 M	-1	1.23	1.23	100
		100.00		

CHEMICAL ANALYSES

The results of chemical analyses of different size fractions are given in Table 5.

Table 5. Chemical Analysis of a Representative Sample of High-MgO Pebble.

Size	Wt. %	P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3
+3/8 in	11.62	19.86	32.23	4.02	0.93	0.52
-3/8+3.5 Mesh	65.36	21.25	36.34	3.43	1.145	0.84
-3.5+6 M	18.14	17.09	27.92	2.34	1.32	0.86
-6+9 M	2.05	24.32	38.90	2.75	1.08	1.17
-9+16 M	1.6	20.42	28.71	2.12	1.27	1.07
-16 M	1.23	13.62	22.75	2.44	1.13	0.95

Since most of the rock was relatively coarse, a portion of it was crushed and re-screened to obtain smaller fractions that could be used in the tests.

FLOTATION TESTS

Effect of Acid Type

Different acids (H_2SO_4, HCl, HNO_3, and acetic acid) were used. The inorganic acids HCl, HNO_3, and H_2SO_4 gave the same results at 2% acid concentration. On the other hand, acetic acid (RCOOH) formed a very small number of bubbles at 2% acid concentration. Increasing the concentration of acetic acid to 5% gave no significant variation in bubble formation, which means that the organic acids are too weak and would require large amounts to be compared with inorganic ones.

Effect of Acid Dosage

Since all the inorganic acids behave in the same manner, sulfuric acid was selected for the rest of the experiments since it is the least expensive and is already widely used in the industry. Table 6 shows the effect of acid concentration on the bubble formation rate, amount of bubbles formed, and particle floatability. These were used as the criteria for comparing the results.

Table 6. Effect of Sulfuric Acid Concentration on Bubble Formation on Dolomite Particles Coated with SDS (Dipped into 1.0% Solution of SDS) Before Transferring to the Acidic Solution.

	Sulfuric Acid Concentration				
	0 %	0.25 %	0.5%	1%	2%
Bubble formation rate	Very slow	Slower than 5%	Slow	Fast	Rapid
Amount of bubbles formed	Very small number of bubbles (about 5 bubbles for 10 min. then no bubbles formed)	The interval between formation of two bubbles was about 30 sec.	Increased rate and number of bubbles formed	Continuous formation of bubbles but at rate higher than 0.5%	Continuous and quick formation of many bubbles
Flotation of dolomite particles	No flotation	No flotation	No flotation	Floated after 5-10 min.	Floated after 1 min.

In Table 6, we can note that the reaction between dolomite and acid to produce CO_2 decreases noticeably with decreasing acid concentration and the flotation of

dolomite particles takes a longer time (5-10 minutes) in 1% acid than the flotation in 2% acid. Consequently, the 2% sulfuric acid concentration is the most suitable acid concentration for bubble formation in terms of bubble formation rate and quantity of bubbles formed. But because of the wide gap between 1% and 2% acid concentration, another set of experiments was conducted, as shown in Table 7, to get the optimum acid concentration.

Table 7.   Effect of Sulfuric Acid Concentration on the Bubble Formation Rate on Dolomite Particles Dipped into1.0% SDS Solution Before Transferring to the Acidic Solution.

	Sulfuric Acid Concentration					
	1 %	1.2 %	1.4%	1.6%	1.8%	2.0%
Bubble formation rate	Rate increased with increasing acid conc. %					
Amount of bubbles formed	Continuous and small number of small bubbles	Number of bubbles increased with increasing acid concentration				Continuous and large number of small bubbles
Flotation of dolomite particles	Particles floated after 20 minutes, but were not stable (particles went up and down)	Particles floated and stayed at interface for 5 min., then went back to the solution for 2 min., then went up again		Particles floated and stayed at interface		Floated and stayed at interface

Table 7 shows that the flotation at 1% and 1.2% is not stable and flotation occurs after the particle loses part of its weight due to reaction with the acid. Thus this concentration works with small particles (smaller than 1mm) rather than large particles. The bubble formation rate decreases with decreasing acid concentration from 2% to 1%, but the difference is narrower, between 1.6-2%, so a 1.6% acid concentration was determined to be optimum. Also, the same observation was made with Mr. Bubbles® solution, i.e., that 1.6% was the optimum acid percentage.

Effect of Surfactant Type

Table 8 shows the observations made when anionic, cationic and nonionic surfactants are tested in a 2% sulfuric acid solution. The performance was in the following order: Anionic> Nonionic> Cationic. Anionic surfactants formed stable "membranes" that captured CO_2 and persisted for 10 minutes. Anionic surfactants are the best, especially $SDSO_3$. Therefore, $SDSO_3$ was used in the next experiments.

Table 8. Preliminary Tests of High Dolomitic Phosphate Coated with (Dipped into) Different Surfactants.

Surfactant Name	Remarks
Arquad® 12-50 (1%)	No precipitation of surfactant, stable bubbles for 20-30 sec., particles 2-3 mm could float
Lilamin® (1%)	No precipitation, less stable bubbles for 10 sec., particles did not reach the surface of the solution (air-water interface)
Armac® HT (1%)	Precipitation of surfactant
Armid® HT (1%)	Precipitation of surfactant
Armeen® 12 D (1%)	Precipitation of surfactant
Ethofat® (1%)	Formation of bubbles on the particle surface, then particles floated
$SDSO_3$ (1%)	Bubbles formed and went up to solution surface, but particles didn't float
$SDSO_4$ (1%)	Bubbles formed and went up to solution surface, but particles didn't float
$SDSO_3$ (2%)	Particles took 2-3 seconds to float
$SDSO_4$ (2%)	Flotation rate was slower than when $SDSO_3$ was used
Oleic acid	Added as-is, particles stayed at the surface of the solution (air-water interface) with the formation of many small bubbles
	Common Observations for Nonionic Surfactants Are:
Arlacel®	No significant change in behavior of different nonionic surfactants used
Span®-20	Flotation of high dolomitic particles after 3-5 seconds and they stayed at the surface, while the low dolomitic particles did not float
G-1096	Formation of stable bubbles on the floated particle surface
Brij® 97	
Arlatone® T	
Tween® 21	
Tween® 85	

Effect of Surfactant (SDSO$_3$) Dosage

The results of different dosages of the surfactant SDSO$_3$ are shown in Table 9. The effects of coating particles with surfactant before transferring them to the acidic solution are detailed in the same table.

Table 9. The Effect of Surfactant Concentration (SDSO$_3$ - 2% Is Used to Coat Particles and Is Added to the Acidic Solution to Achieve the Different Concentrations Indicated).

	SDSO$_3$ Concentration in Acidic Solution		
	0.04%	0.08%	0.12%
Particles without any coating	• Many bubbles formed • small particles (1-2 mm) floated; • large particles (3-4 mm) went up and down	• Many bubbles formed • Small particles (1-2 mm) floated • Large particles (3-4 mm) floated • Floatability at 4% SDS was more stable than at 2% & 6%	• Many bubbles formed • Small particles (1-2 mm) floated • Large particles (3-4 mm) floated
Particles coated with SDSO$_3$	• Many bubbles formed • Small particles floated • Large particles did not float	• Many bubbles formed • Small particles floated • Large particles did not float	• Many bubbles formed • Small particles floated • Large particles did not float

It is indicated in Table 9 that particles without coating (without immersing into surfactant before adding the particles to the acidic surfactant solution) form bubbles quickly, in large quantities, and their flotation rate is higher than that for particles immersed in surfactant before their addition to the acid. This may be due to the absence of a surfactant layer that prevents instantaneous contact between the particle surface and the acidic solution.

Increasing the surfactant concentration increases the floatability of the particles and large particles (3-4 mm) can float at high surfactant concentrations up to 0.08%. After that, there is no noticeable change in floatability, i.e., 0.12% is closely similar to 0.08%.

Effect of Particle Size Using SDSO$_3$ as the Surfactant

The results of tests conducted to investigate the role of particle size in the formation of bubbles and efficient flotation are given in Table 10. The effect of coating

particles with surfactant before transferring them to the acidic solution is presented in Table 10 below.

Table 10. Effect of Particle Size on Dolomite Floatability in a 2.0% Acidic Solution Containing 2.0% SDSO₃.

	0.5-1 mm	1-2 mm	2-4 mm	4-6 mm
Without coating with surfactant solution	• Particles floated and stayed at water/air interface	• Particles floated for few seconds then oscillated (up and down)	• No flotation, but the particles went up and down. They did not reach the interface.	• No flotation, but sometimes particles floated for 2 sec. and then sank down.
Coated with surfactant solution	• Slow rate, took time to float. Finally floated and stayed at interface.	• Floated after 30 sec. and stayed at water/air interface	• Went up and down and finally stayed at water/air interface	• Floated after 1 min., then went up and down for 5 min.

Table 10 indicates that coating particles with surfactant (immersing them in 2% surfactant solution) affects the stability of the floated particle at the interface; however, uncoated particles release more bubbles and float faster, which leads to the presence of uncoated particles at the interface for a shorter time than coated ones. With large size particles, the formed bubbles are not enough to lift the particles, so the particles oscillate up and down.

Oil-Surfactant Experiments

Addition of an oil layer, vegetable or corn oil, to the acidic solution/air interface was used with different types of surfactants to enhance the bubble stability at the interface, as shown in Tables 11A to 11C.

Table 11A. 2% Sulfuric Acid Solution + 0.5 cm Oil Layer. Particles Are Dipped into a 2.0% Surfactant Solution Before Being Transferred to the Acidic Solution.

Surfactant	Type	Observation
Arquad® Lilamin®	Cationic	Formation of bubbles due to dissolution of dolomite, but the particles did not float.
Ethofat®	Anionic	Bubble formation Particles floated to water/oil interface for 10 min. and then returned back to water.
SDSO₃ SDSO₄		Bubble formation on particle surface Particles floated to water/oil interface for about 10 min. and then returned back to water.

Table 11B. 2% Sulfuric Acid + 1% Surfactant. Particles Are Dipped into a 2.0% Surfactant Solution Before Being Transferred to the Acidic Solution.

Surfactant	Type	Observation
Arquad® Lilamin®	Cationic	Formation of cluster of bubbles on particle surface due to dissolution of dolomite, and the particles did not float.
Ethofat®	Anionic	Bubble formation and particles fluctuating between the water/air interface (where the bubble breaks), and the bottom of the beaker.
SDSO$_3$ SDSO$_4$		

Table 11C. 2% Sulfuric Acid + 1.0 % Surfactant + 0.5 cm. Oil Layer. Particles Are Dipped into a 2.0% Surfactant Solution Before Being Transferred into the Acidic Solution.

Surfactant	Type	Observation
Arquad® Lilamin®	Cationic	Formation of bubbles due to dissolution of dolomite, but the particles did not float. Precipitation of Lilamin in acidic solution.
Ethofat®	Anionic	Bubble formation on particle surface. Particles did not float.
SDSO$_3$ SDSO$_4$		Bubble formation on particle surface and particles floated to water/oil interface, then to oil/air interface.

It is clear from Table 11A that the oil layer makes the bubbles formed on the particles more stable. When the particles float to the water/oil interface, the floated particles stay at the interface for up to 10 minutes.

From Table 11B, one can observe that the presence of a low percentage of surfactant (1%) in the acidic solution slightly affects the stability of the bubbles in the absence of an oil layer at the interface.

By using an acidic solution in combination with a 1% surfactant and an oil layer, as shown in Table 11C, we found that the oil layer made the bubbles formed on the particles more stable when the particles float to the oil/air interface. These particles do not go back into the acid solution but stay at the oil/air interface. Consequently, large particles up to 3 mm can float in the presence of the surfactant and oil layer.

SDS is a good surfactant under these experimental conditions. However, Ethofat and cationic surfactants did not work well in the presence of a surfactant mixed with the acidic solution. This may be due to the interaction between the oil layer on the particles and these surfactants.

Effect of Mr. Bubbles® as a Surfactant

Commercially available Mr. Bubbles® solution (available in toy stores for blowing bubbles*) was used due to its known ability to form stable bubbles in air. The results of using Mr. Bubbles® were promising, as is shown in the following tables.

It is obvious from Table 12 that the floatability of particles increases with increasing Mr. Bubbles® concentration. Large particles (3-4 mm) can float starting from a 4% Mr. Bubbles® concentration with good stability at the interface (they remain at least 10-20 minutes). Increasing the concentration to more than 4% gives no noticeable change in floatability. It was also noticed that there was no floatability of low-dolomite particles, even though a large number of bubbles formed on the surface of those particles. Therefore, a 4% Mr. Bubbles® solution was used in the next experiments.

Table 12. Effect of Mr. Bubbles® Concentration on Dolomite Particle Flotation in a 1.6% Sulfuric Acid Solution.

	Mr. Bubbles® Concentration						
	0.5 %	1%	2 %	4%	6%	8%	10%
Particles without coating	Flotation of particles(<0.5-1 mm) and oscillation of particles (>1 mm)	Flotation of particles (up to 4 mm) but larger ones (3-4 mm) stayed at the interface no longer than 30 sec	Flotation of different sizes (between 0.5-4 mm)				
Particles coated with Mr. Bubbles® solution	Their ability to float was slower than without treatment						
Flotation of dolomite particles	Took about 3 min.	Took about 1-2 min.	Took about 30 sec.	Did not touch the beaker bottom (fast flotation)			
Stability of floated particles at interface	Unstable and oscillated	Slightly stable	Stable	Stable			

By testing different particle sizes, as shown in Table 13, the flotation rate of small particles is higher than that of coarser ones. However, there is only a few seconds difference in the flotation of same-size particles with or without treatment with Mr. Bubbles®.

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*This product, Mr. Bubbles®, should not be confused with Mr. Bubble®, which is a registered trademark of Playtex Products, Inc. and is a bubble bath formulation.

Table 13. Effect of Particle Size on the Floatability and Stability of the Particles at the Water/Air Interface (Using 1.6 % Sulfuric Acid + 4.0% Mr. Bubbles®).

	0.5-1 mm	1-2 mm	2-4 mm	4-6 mm
Without coating	Particles floated and stayed at water/air interface	Particles floated and stayed at water/air interface	Particles floated and stayed at water/air interface	Particles floated and stayed at water/air interface
With coating	Particles floated and stayed at water/air interface	Particles floated and stayed at water/air interface	Particles floated and stayed at water/air interface	Particles floated and stayed at water/air interface

Effect of Latex Paint as a Coating Agent

One of the suggested ideas was to use latex paint as a coating agent to float dolomitic particles. The particles were coated with latex paint and allowed to dry for 1 to 1.5 hours before adding them to an acidic solution with no surfactant present. The high-dolomite particles floated and there was no flotation of low-dolomite particles (floated particles stayed at the water/air interface for a limited time, not more than 5 minutes).

Effect of Rubber Cement as a Coating Agent

Rubber cement was also used in floating dolomite particles, as it was expected to form a flexible membrane on the dolomitic particles and lead to their flotation. Several experiments were conducted. By using 3% H_2SO_4 and coating the particles with rubber cement, large bubbles were formed, but as separate bubbles (not covering all the particle surfaces as in the PVA case discussed below). However, no flotation of the particles occurred within 45 minutes except for flaky particles (2 mm size). A few of these small particles floated to the surface and dropped down just after reaching the interface.

In addition, surfactants like Mr. Bubbles®, Ethofat®, $SDSO_3$, and Arquad® amine were added to the acidic solution to enhance bubble formation, bubble stability, and flotation rate, but the results were not promising due to the interaction of the rubber cement with the surfactant in the acidic solution. Therefore, no stable bubbles formed and no flotation of particles occurred.

Effect of Polyvinyl Alcohol (PVA) as a Surfactant

PVA was used as a viscous polymer to coat and float the dolomite particles. The effect of acid concentration percentage, different particle sizes, and different PVA percentages were studied.

PVA forms a membrane on the particles. This membrane needs a high acid concentration to penetrate it and to perform the reaction between the acid and the particle surfaces, as it was observed that there was a very small number of generated bubbles. However, most of the bubbles formed a cluster on the surface of the particles, which increased the volume of the bubbles at the surface and floated the particles. The floated particles were not stable at the beginning, went up and down and finally stayed at the interface for a long time (sometimes more than 2 days). On the other hand, PVA floated the low-dolomite particles, which are able to form bubbles. We observed this only with PVA, which makes it the best choice.

By increasing the PVA concentration, a longer time was taken to form bubbles and float the particles. This required a higher acid concentration, but in this case large particle sizes can float (up to 8 mm).

Table 14A. Effect of Acid Concentration on Flotation of PVA-Coated Particles (Dipped into a 2.0% PVA Solution Before Transferring to the Acidic Solution).

	Acid Concentration, %			
	0.5	1.0	1.5	2
Particles coated with PVA	• Formation of cluster of bubbles • Very low bubble formation rate • No particle flotation (up and down at 1.5%)			• Cluster of bubbles formed • Low bubble formation rate • Particles floated

In Table 14A, the data indicate that the PVA formed a membrane on the particle. This membrane needs a high acid concentration to penetrate it and to perform the reaction between the acid and the surface of the particles to release the gas which is responsible for floating the particle. At low acid concentrations, a very small number of bubbles were generated and the rate of bubble formation and particle flotation was very slow. After several minutes, most of the bubbles formed a cluster on the surface of the particles, which increases the overall gas volume adhering to the surface and allows the particles to float.

Also, at low acid concentration, the floated particles were not stable, i.e. they went up and down. However, at a high acid concentration, the acid took time to penetrate the PVA membrane and react with the surface of the particles. For that reason, the

bubble formation rate was low. But after the bubbles formed and covered the surface of the particles in a cluster, the particles started to float.

An acid concentration of less than 2% was not effective due to the high viscosity of the PVA membrane.

Another set of experiments was conducted at a higher acid concentration (> 2%). Table 14B shows the results of those experiments.

Table 14B. Effect of Higher Acid Concentration on Bubble Formation and Flotation of PVA-Coated Dolomite Particles.

	Sulfuric Acid Concentration			
	2.5 %	3%	3.5%	4%
Bubble formation rate	Increases with increasing acid conc. %			
Amount of bubbles formed	Cluster of bubbles formed on the particle surfaces			Rapid reaction, no stable bubbles were seen on the surface (bubbles were released at a high rate from particle surfaces)
Flotation of dolomite particles	• Particles floated • Was more stable than higher acid conc.		• Particles floated • Less stable than 2.5-3%	• Particles did not reach the surface (oscillated) and finally went down

There was no flotation at acid concentrations above 3% due to the high bubble formation rate and the absence of stable bubbles that could attach to the surface of the particles and float them. The bubble formation rate increased with increasing acid concentration, 4 % > 3.5 % > 3 % > 2.5%; however, a concentration of 2.5-3% gave the most stable bubbles on the particles coated with PVA.

Different PVA concentrations were used (2%, 3%, and 4%) and the experiments indicated that a concentration of 3-4% was the most suitable for dolomite flotation. However, the increase in PVA concentration increased the time required to float the particles.

Effect of Particle Size on Flotation of PVA-Coated Dolomite Particles

Larger particle sizes require a longer time to generate enough gas to float the particles. This can be explained by the decrease in surface area to the weight of the particles, which decreases with increasing particle size. The results of these tests are shown in Table 15.

Table 15. Effect of Particle Size on PVA-Coated Dolomitic Particles During Flotation in 2.0 % Acidic Solution.

	Particle Size, mm		
Particles coated by PVA	0.5-1	1-2	2-4
	Floated in 10 minutes	Floated in 30 minutes	Floated in 60 minutes
	Increasing particle size increased the time needed for particle flotation		

Effect of Adding PVA to the Acidic Solution Versus Coating the Particles with PVA

By using two beakers, one of them containing PVA and acid (particles not coated with PVA) and the second containing just acid (but particle coated with PVA), a comparison can be made between the performance of PVA in the two beakers. Table 13 shows the results in terms of bubble formation, rate of formation, and particle flotation.

Table 16. Comparison Between Coating the Particles Before Adding Them to a 3.0% Acidic Solution and Adding the Particles to a 3.0% Acid+ 0.12% PVA Solution Without Coating.

	First Beaker	Second Beaker
	PVA + acidic solution in the beaker and the particles added without coating	Coating the particles with PVA before adding them to the acidic solution
Bubble formation rate	Tiny bubbles were formed	Relatively large bubbles were formed
Amount of bubbles formed	Cluster of the bubbles grew vertically and covered parts of the particle surface – no uniform distribution of the bubbles on the particle surface	Cluster of the bubbles grew almost horizontally and was uniformly distributed on the particle surface
Flotation of dolomite particles	Took a long time (hours) to float	Took a short time (minutes) to float

In the first case where uncoated particles were dropped into the PVA acidic solution, the acid attacked the surface of the particles and consequently the dissolution of dolomite was higher than in the case of coating the particles with PVA before adding them to the acidic solution. The presence of microbubbles (cotton-shaped) at the particle surface indicated the dissolution of dolomite.

Bubbles were vertically distributed rather than horizontally, as they were in the first beaker, while the bubble distribution was horizontally uniform (spreading on the PVA-coated particle surface) in the second beaker. The bubble formation rate was higher in the first case than in the second. However, the flotation of the particles was better in the second case due to the presence of relatively large bubbles and uniform bubble distribution. The flotation of the particles in the first case took a long time because of the small size of the bubbles. Also, it took some time for the dissolution of the dolomite particles until their size was such that they could float with such small bubbles. The floated particles in both cases stayed at the interface for a long period of time (a matter of days).

Flotation of a Representative Sample

A representative rock sample, i.e. a mixture of phosphate and dolomite, was floated in a one-liter beaker. The floated fraction wt% was about 22% and the unfloated fraction was 78% after six hours.   It was noticed that the smaller particle sizes (less than 1 mm) floated immediately. Therefore, using a small size fraction of about 1 mm with PVA will reduce flotation time with a very low chance of dissolving the particles due to good PVA coating, which prevents rapid acid-attack to the particles. On other hand, we should take into account that PVA consumption will increase due to the increase in surface area.

Separation Flotation of a Fraction of Representative Sample (-4+1.19 mm) in an Acidic Solution Containing PVA

A bucket (11 inches in diameter and 15 inches in height) containing 15 liters of water, 3% sulfuric acid, and 200 ppm PVA was used. The water height in the bucket was about one foot. The quantity of rock added was 150 grams. Most of the particles were in a monolayer on the bottom of the bucket to avoid mechanical entrapment of particles. Results are shown in Table 17. The data indicate that MgO is reduced to less than 1% in the sink fraction. The P_2O_5 in the floated fraction is less than 4%.

Effect of Time on Separation Flotation of PVA-Coated Dolomite Particles

Two rock samples of - 4+1.19 mm size were tested in the bucket device described in the previous test, but using shorter test times (30 minutes, 60 minutes). The samples were immersed in a 3% PVA solution and mixed to ensure the coating of all particles with PVA before adding the sample to acidic water (3% sulfuric acid). Each experiment was observed for two days and the floated fraction was collected. Most of the particles (about 90%) floated through 30 minutes and about 10% in the rest of the two days of the experiment. The results are shown in Table 18. It is clear that the MgO is reduced to about 0.8%. The P_2O_5 is less than 1% in the float fraction, which indicates that the use of PVA could be a promising process for separation of dolomite from phosphate pebbles.

Table 17. Separation Flotation of Dolomite from a Representative Sample (Results of -4+1.19 mm Particle Size).

Sample	Wt%	Chemical Analysis, %				Recovery, %			
		MgO	CaO	P_2O_5	I.R.	MgO	CaO	P_2O_5	I.R.
Float	14.55	13.21	32.56	2.71	6.89	75.1	13.73	2.33	10.01
Sink	85.45	0.75	34.83	19.35	10.55	24.9	86.27	97.67	89.99
Balance	100	2.56	34.50	16.93	10.02	100	100	100	100
Feed	100	2.6	34.78	16.84	10.32	100	100	100	100

Table 18. Results of Separation Flotation of –4+1.19 mm Particles.

Time	Size, mm		Wt%	Chemical Analysis			Recovery		
				MgO%	CaO%	P_2O_5%	MgO%	CaO%	P_2O_5%
30 min.	-4+1.19	Float	16.75	13.62	24.25	0.76	77.84	13.55	0.8
		Sink	83.25	0.78	31.12	18.89	22.16	86.45	99.2
		Balance	100	2.93	29.97	15.73	100	100	100
		Feed	100	3.03	30.38	15.76	100	100	100
60 min.	-4+1.19	Float	17.44	13.6	26.17	0.94	78.0	15.22	1.03
		Sink	82.56	0.81	30.8	19.06	22.0	84.78	98.97
		Balance	100	3.04	29.99	15.90	100	100	100
		Feed	100	3.03	30.38	15.76	100	100	100

Effect of Particle Size on the Separation Flotation of PVA-Coated Particles

Two samples were crushed in a closed circuit to obtain the following sizes: -4 +1.19 mm, -3.36+1.19mm. The test conditions were the same as in the previous two tests. The results of these tests are shown in Table 19. The data suggest that the MgO is reduced to less than 1% (to 0.6% in the unfloated fraction in the first experiment and to 0.95% in the second). The CaO % is approximately the same in the sink and float. The P_2O_5 in the floated fraction is less than 4%.

Table 19. Effect of Particle Size on Separation Flotation of PVA-Coated Particles.

Size, mm	Sample	Wt %	Chemical Analysis, %				Recovery, %			
			MgO	CaO	P_2O_5	I.R.	MgO	CaO	P_2O_5	I.R.
-4+1.19	Float	20.5	12.13	30.34	3.31	8.1	83.9	20.55	4.27	17.87
	Sink	79.5	0.6	30.24	19.13	9.6	16.1	79.45	95.73	82.13
	Balance	100	2.96	30.26	15.89	9.29	100	100	100	100
	Feed	100	3.03	30.38	15.76	9.46	100	100	100	100
-3.36+1.19	Float	17.8	11.84	34.53	3.86	7.04	72.96	16.43	4	12.84
	Sink	82.2	0.95	38.02	20.07	10.35	27.04	83.57	96	87.16
	Balance	100	2.89	37.40	17.18	9.76	100	100	100	100
	Feed	100	2.95	37.07	17.41	9.93	100	100	100	100

Flotation in Pond Water

A sample of pond water containing about 1% sulfate and 2% P_2O_5 was evaluated as a possible substitute for the sulfuric acid solution. These experiments were conducted on dolomite particles only. The results indicated that the pond water was not as good as the sulfuric acid solutions with regard to bubble formation, bubble formation rate, and particle flotation.

Analytical Problems

All the analyses were performed at the ERC using ICP (as is used throughout the industry). Since the P_2O_5 in the sink fractions appeared to be low, several samples of the floated and non-floated pebbles were sent to IMC to determine if there were analytical errors. While there was general agreement on the insol, CaO, Fe_2O_3 and Al_2O_3, the IMC results showed about 10% more P_2O_5 and 20% higher MgO.

After comparing the methods used by the laboratories, the problem was found to be the method of calibration. At the ERC, pure components were used for the calibrations, while the industry uses a rock check sample. Since there is a matrix effect with phosphate and magnesium, use of the rock check sample gives the more accurate results.

Additional Analyses

Even after the upward adjustments in phosphate and magnesium, the total analyses seemed low. IMC was requested to run the sulfate and carbonate on the samples shown in Table 19. While the carbonate analyses were consistent with the MgO analyses, the sulfate analyses of all samples were 6-14% (0.8% is typical for Florida pebble), indicating the presence of calcium sulfate. When the non-floated samples were corrected for the dilution effect of the calcium sulfate, the BPL of these fractions increased to 64.24 and 62.58, which is consistent with rock containing 1-2% MgO.

The presence of the high quantity of calcium sulfate (15.7% and 26.6%) is the result of the 24-hour exposure to the 3% sulfuric acid solution. While it is expected that the quantity of calcium sulfate would be reduced by shorter exposure times, it is not necessarily bad. Any calcium that reacts with the acid in this process is less calcium that would be available to react with the sulfate in the phosphoric acid attack tank.

Separation Coefficients

The separation coefficients for the tests given in Tables 17-19 are 126, 434, 340, 117, and 65 based on the ERC analyses. The last two are 79 and 70, based on the IMC

analyses. Clearly the process generates separation coefficients in excess of 50 compared to about 4 for the heavy media separation and 20 for the CLDRI process.

Separation Efficiency

The separation efficiency for the tests given in Tables 17-19 are 86.4, 88.5, 88.4, 89.8, and 84.5% based on the ERC analyses. The last two are 86.4 and 83.7 based on the IMC analyses. Clearly the process generates separation efficiencies in excess of 80% compared to 55-70% for the heavy media separation and 75-80% for the CLDRI process.

CONCLUSIONS

Dolomite can be separated from apatite by coating it with a surfactant and immersing it in a dilute acid solution where the dolomite will generate carbon dioxide gas that is trapped by the surfactant and floated to the surface.

PVA (polyvinyl alcohol) is the best surfactant found to date for coating the mixture of phosphate rock and dolomite.

Separation coefficients for the process are greater than 50 compared to about 4 for the heavy media separation process and about 20 for the CLDRI process.

This process will work on pebble-size rock of up to 8-10 mm in size.

The separation efficiency is greater than 80%.

RECOMMENDATIONS

This process should be explored further to determine the best method of continuous application and ultimately the process economics. Specific areas that need to be addressed are:

- What is the consumption of PVA?
- Will PVA cause any downstream problems?
- How much sulfuric acid will be consumed?
- Should the rock be crushed (to speed up the process) or the larger particles eliminated by screening?
- How should the PVA be applied?
- What should the flotation process look like?
- What are the economics?
- What is the demonstrated performance on a wide variety of rock sources?

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