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Removal of Magnesia From Dolomitic Southern Florida Phosphate Concentrates by Aqueous SO₂ Leaching

By J. P. Hansen, B. E. Davis, and T. O. Llewellyn



UNITED STATES DEPARTMENT OF THE INTERIOR



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	UNIT OF MEASURE ABBREVIATI	ONS USED IN	THIS REPORT
°C	degree Celsius	mL/min	milliliter per minute
g	gram	min	minute
h	hour	μm	micrometer
in	inch	pct	percent
1b	pound	t	metric ton
1b/ton	pound per ton	wt pct	weight percent
mL	milliliter		

REMOVAL OF MAGNESIA FROM DOLOMITIC SOUTHERN FLORIDA PHOSPHATE CONCENTRATES BY AQUEOUS SO₂ LEACHING

By J. P. Hansen, ¹ B. E. Davis, ² and T. O. Llewellyn ³

ABSTRACT

The Bureau of Mines has investigated the SO_2 leaching of MgO from high-MgO-bearing Florida phosphate concentrates. The SO_2 was effective in leaching some of the MgO from three phosphate concentrates; flow rate of the SO_2 and leach time were major factors in determining the amount of MgO leached. Calcining the samples, then grinding to minus 200 mesh, and elevating the leach temperature gave only small increases in the amount of MgO leached.

The research also showed that some of the MgO was so intimately associated with the phosphate mineral that it could not be removed by SO_2 leaching. This amounted to about 0.6, 0.7, and 1.0 pct MgO in three leached residues. The calculated heads for the three concentrate samples averaged 1.4, 1.1, and 1.5 pct MgO, respectively, before leaching.

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Production of phosphate rock in the United States has historically increased annually and in 1980 amounted to about 54 million t. The combined production from the Florida mines and the single mine in North Carolina was 87 pct of the U.S. production (1).⁴ In 1980, land pebble phosphate was produced at 22 mines in Hamilton, Hardee, Hillsborough, and Polk Counties, in central Florida (2). In the United States, wet-process phosphoric acid accounted for about 85 pct of domestic consumption.

As phosphate mining moves south into Hardee and Manatee Counties, lower grade ore bodies with lesser amounts of coarse pebble and higher MgO content are encountered. The higher MgO content of the phosphate concentrates may result in problems during acidulation with H_2SO_4 . The carbonate minerals increase the H_2SO_4 and defoamer requirements and lower the P_2O_5 production rate (3). In addition, gypsum filtration is generally difficult at over 0.5 pct MgO. An insoluble magnesium salt also may precipitate and settle in the phosphoric acid during shipment and storage, which creates handling problems and lowers the $P_{2}O_{5}$ content of the finished product (4).

Bureau of Mines research has shown that sulfurous acid (SO2) can be used to remove MgO from western phosphate concentrates (5). SO2 also rapidly leached part of the MgO from Pacific sea nodules (6). Solutions containing 5.6 pct SO_2 leached 63 to 67 pct of the MgO in 10 min, while 6.4- and 8.9-pct-SO2 solutions leached 72 to 74 and 80 to 82 pct of the MgO. This report presents results on studies to reduce the MgO content of several phosphate concentrates. Lowering the MgO content to below 0.5 pct would be desirable to permit acidulation of the phosphate concentrate without the formation of insoluble magnesium precipitates.

DESCRIPTION OF SAMPLES

Three samples of high-MgO phosphate concentrate were used in this study. The first sample was produced by batch flotation from matrix from the Bone Valley Formation in Manatee County, FL. The matrix, obtained from a commercial drilling firm, had chemical analyses, in percent, as follows: 6.8 P205, 19.1 Ca0, 4.6 Mg0, 54.7 insol, 10.1 CO₂, 0.8 F, 0.9 Fe₂O₃, and 0.7 Al_20_3 . The matrix was ground to pass 35 mesh, deslimed at 150 mesh, and conditioned with 1.0 1b of sodium carbonate and 1.5 1b of fatty acid-fuel oil combination (2 parts fatty acid to 3 parts fuel oil) per ton of flotation feed (7). The rougher concentrate was cleaned three times using 1.0 1b of sodium silicate per ton of flotation feed in each cleaning stage to depress the silica. The cleaned concentrates were used for leaching.

The second sample was a pilot plant flotation concentrate obtained from a phosphate company.

The third sample was a pilot plant flotation concentrate produced at the Bureau of Mines Tuscaloosa Research Center from a dolomitic phosphate ore obtained from southern Florida (8). The rougher concentrate was produced using fatty acidfuel oil, sodium carbonate, and frother and recleaned three times. The chemical analyses of the three concentrates are shown in table 1, and the screen analyses are shown in table 2.

TABLE 1. - Chemical analyses of samples, percent

	Sample 1	Sample 2	Sample 3
P ₂ 0 ₅	29.5	29.3	30.7
Ca0	46.9	45.5	49.6
Mg0	1.22	1.1	1.3
Al ₂ 0 ₃	.76	.81	1.0
Insol	2.98	6.0	2.5

⁴Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Size, mesh	Sample 1	Sample 2	Sample 3
Plus 14	0	2.4	0
Minus 14 plus 20	0	7.1	0
Minus 20 plus 28	0	12.2	0
Minus 28 plus 35	0	17.8	10.9
Minus 35 plus 48	36.6	24.9	37.5
Minus 48 plus 65	30.2	21.9	29.0
Minus 65 plus 100	20.8	10.5	15.6
Minus 100	12.4	3.2	7.0
Total	100.0	100.0	100.0

TABLE 2. - Screen analyses of samples, weight percent

PETROGRAPHIC ANALYSES OF SAMPLES

Triplicate thin sections were prepared for each size fraction of the three concentrates shown in table 2 for petrographic examination.⁵ It was expected that the MgO-bearing minerals could be guide characterized to the leaching strategy. Dolomite, the only MgO-bearing mineral identified, occurred in three primary forms: Type 1 was individual dolomite grains or aggregates of smaller dolomite grains, type 2 was partially phosphatized dolomite aggregates, and type 3 was individual grains that were inclusions in the phosphate mineral grains.

The dolomite from sample 3 appears in various shades of white in figure 1. Type 1 is typically a large dolomite grain, but other smaller type 1 grains and aggregates of dolomite grains are seen. Type 2 is a partially phosphatized dolomite aggregate; the individual grains appear in different shades because of differences in degree of phosphatization. Type 3 is dolomite imbedded in the phosphate grains; the crystals are often rhombs, which are a solid form bounded by three parallel pairs of rhombus-shaped faces, which is a common dolomite shape.

The type 1 dolomite aggregates are masses of 10- to $50-\mu$ m dolomite rhombs. Most are of uniform composition, though

⁵The petrographic analyses and the photograph in figure 1 were prepared by Dr. D. J. Benson of the Geological Department at the University of Alabama. some are zoned with dark cores and clear rims. Studies indicated that the dolomite is a high-Mn, low-Fe dolomite, and the texture and composition suggest the dolomite is derived from a dolostone lithology in the host rock.

The type 2 dolomite in the partially phosphatized aggregates is similar to that in the type 1 aggregates, indicating that they represent partially altered type 1 material.

The type 3 dolomite is very different from types 1 and 2. The type 3 dolomite is coarser grained and is commonly zoned. The dolomite occurs as isolated rhombs floating in a phosphate matrix. This suggests the type 3 dolomite originated as scattered replacement rhombs in a limestone matrix. The limestone may have been replaced by phosphate while the dolomite rhombs remained.

Table 3 shows the percentage of type 1 dolomite in each size fraction of the three samples as determined by grain count. The percentages shown are percent dolomite, so the actual MgO percentage is 0.22 of the amount shown. Only the type 1 dolomite aggregates were determined; thus both the total dolomite content and the total MgO content are higher than the percentages shown.

The petrographic analysis in table 3 indicates that sample 1 averages 6.26 pct of type 1 dolomite, or 1.38 pct MgO, which should leach completely. Sample 2 averages 2.25 pct type 1 dolomite, or



FIGURE 1. - Photomicrograph showing types 1, 2, and 3 MgO minerals (X 80).

Mesh, size	Wt pct Run 1		Run 2		
		Analysis, pct	Units ¹	Analysis, pct	Units ¹
	-	SAMPLE 1			
Plus 48	36.6	2	0.73	2.33	0.85
Minus 48 plus 65	30.2	5	1.51	8.33	2.51
Minus 65 plus 100	20.8	10.5	2.18	9.66	2.01
Minus 100	12.4	8.5	1.05	13.67	1.69
Composite	100.0	5.47	5.47	7.06	7.06
		SAMPLE 2			
Plus 14	2.4	1	0.02	1.33	0.03
Minus 14 plus 20	7.1	2	.14	1.00	.07
Minus 20 plus 28	12.2	1	. 12.	3.33	- 41
Minus 28 plus 35	17.8	3	.53	2.66	•47
Minus 35 plus 48	24.9	1	.25	1.66	.41
Minus 48 plus 65	21.9	2.5	.55	1.33	.29
Minus 65 plus 100	10.5	5	.53	5.33	• 56
Minus 100	3.2	3.5	.11	0	0
Composite	100.0	2.25	2.25	2.25	2.25
		SAMPLE 3			
Plus 35	10.9	4	0.44	3.6	0.39
Minus 35 plus 48	37.5	5.7	2.14	5	1.88
Minus 48 plus 65	29.0	8.3	2.41	9	2.61
Minus 65 plus 100	15.6	5.7	.89	7	1.09
Minus 100	7.0	8	.56	7	.49
Composite	100.0	6.44	6.44	6.46	6.46

TABLE 3. - Type 1 dolomite content of sized phosphate samples

¹A unit is 1 pct contained dolomite, or 1 g dolomite per 100 g head sample, and is equivalent to 20 1b per ton of ore.

0.50 pct MgO, and sample 3 averages 6.45 pct type 1 dolomite, or 1.42 pct MgO.

Dufour (9) determined from mineralogical investigations that part of the carbonates appear as coalescent particles with other parts disseminated in the clay cement and MgO in the apatite lattice. They concluded that the apatite lattice contained 0.63 pct MgO, which could not be removed by flotation.

DETERMINING SIGNIFICANT VARIABLES

To determine the significance of several processing variables, a partial factorial experiment was designed (10) to test the importance of 7 factors in 16 observations. Table 4 lists the factors and the levels tested. The observations were made using 100 g of sample 1. Results of the experiment were based on the amount of MgO contained in the leach liguor. Main effects were calculated for the seven factors, and it appeared that leach time, SO2 flow rate, calcination, and possibly pulp density were important. To verify the findings, contrast sums were calculated and ranked from lowest to highest absolute value. The contrast sum

versus rank number was then plotted on a half-normal-probability graph (fig. 2). In such a graph, effects that are unimportant should behave as if they came from a normal distribution and plot as a straight line. Conversely, effects that are important should lie off the straight line. Results of the plot show that leach time, SO2 flow rate, and calcination at 700° C are definitely important, and pulp density is probably important. Lowering the pH to 4, varying the particle size from minus 35 to minus 65 mesh, and increasing the temperature to 40° C had no statistically significant effect on the results using sample 1.

Factor	Level			
	Low	High		
Temperature°C	25	40		
Pulp densitypct solids	20	50		
Leach timeh	0.5	2		
SO ₂ flow ratemL/min	10	25		
Particle sizemesh.	Minus 35	Minus 65		
Calcination	No	700° C		
Slurry pH	Natural	4.0		

TABLE 4. - Factors and levels for partial factorial experiment

RATE STUDIES

To improve the utilization of the SO_2 and determine the rate of MgO extraction with time, the following modifications were made in the apparatus shown schematically in figure 3:

1. The reactor size was increased from 500 mL to 1,000 mL.

2. To make room for other sensors, the shaft stirrer was replaced with a magnetic stirrer, which limited the slurries to lower percent solids.

3. A varistaltic pump was installed to remove the SO_2 from the top of the reactor and recycle it through the pulp.

4. A thermometer and a pH electrode were included to continuously monitor the temperature and pH.

5. An Andreasen pipet was added so that samples of lixiviants could be removed periodically for analyses.

The experimental procedure was to place 800 mL of water in the reactor, turn on stirrer and pumps, add 200 g of phosphate concentrate, flush the air from the system with a 100-mL/min flow of N_2 for 5 min, and start the SO_2 flow at a predetermined flow rate. The temperature and pH were recorded periodically, and every 5 min a 10-mL sample of lixiviant was removed for chemical analysis to determine the rate of MgO solution with time.

To determine the effect of SO_2 flow rate, three leaching tests were made on

sample 1; the results are tabulated in table 5 and shown in figure 4. The quantity of MgO removed from the concentrate, in grams of MgO dissolved per 100 g of head sample, is calculated from the analysis of the lixiviant. The three runs of 30-, 50-, and 100-mL/min flow of $S0_2$ gave varying results. The percent MgO in the heads was calculated from the analysis of



FIGURE 2. - Significance of the seven process factors.



FIGURE 3. - Schematic drawing of apparatus.

	S02	flow	Time,		Residue, pct		Mg0
Test	mL/min	lb/ton	min	P205	P205	MgO	leached,
				analysis	recovery	analysis	pct ¹
Head	NAp	NAp	NAp	29.9	100.0	1.29	NAp
1	30	51.4	60	30.4	98.8	1.1	0.46
2	50	85.7	60	30.1	98.7	.69	.75

31.1

TABLE 5. - Leaching results for sample 1

60 Not applicable. ¹Grams of MgO leached per 100-g sample. NAp

MgO in the residue and leach liquor. The calculated head analyses for the three runs were 1.56, 1.44, and 1.50 pct MgO.

171.3

100

3.

The results from 12 leaching tests using sample 2 and a wide variety of test conditions are tabulated in table 6 and

shown in figure 5. All of the tests were of 1-h duration using SO₂ flow rates of 100 mL/min, which is equivalent to 170 lb SO_2 per ton. Grinding the concentrate to minus 200 mesh, as shown in tests 7 and 8, increases the dissolution rate of the

.66

.84

96.1







FIGURE 5. - Quantity of MgO removed during 12 leaching tests. Percent MgO leached is the grams MgO dissolved per 100 g of sample.

MgO and gives the lowest percent MgO in the residue. These results would be expected in that the finer grinding would expose more surface of the MgO-bearing constitutent, which would increase the rate and also permit more to go into solution. However, grinding from 35 to 65 mesh had no statistical effect on sample 1.

		R	MgO		
Test	Test conditions ¹	P205	P ₂ 0 ₅	MgO	leached,
		analysis	recovery	analysis	pct ²
Head	NAp	29.3	100.0	1.15	0
1	Standard	29.8	93.7	•74	.33
2	12.6 g Na sulfite	29.8	95.2	.73	.39
3	14.2 g Na ₂ SO ₄	28.2	93.2	.71	.37
4	Calcined +14.2 g Na ₂ SO ₄	30.5	96.0	.70	.41
5	Calcined	32.1	98.0	.75	.36
6	80 mL acetic acid	29.9	95.8	.68	.34
7	-200 mesh, 80 mL acetic acid	29.7	94.6	.64	•52
8	-200 mesh	29.8	92.3	.63	.45
9	Calcined, 80 mL acetic acid	32.2	98.0	.71	.38
10	40° C	29.5	96.4	.66	.33
11	80° C	29.3	97.5	.48	•40
12	Sulfurous acid	29.8	91.4	.82	• 32

TABLE 6. - Leaching results for sample 2

NAp Not applicable.

¹All leaching tests run at SO_2 flow rates of 100 mL/min for 60 min, which is equivalent to 170 1b SO₂ per ton.

²Grams of MgO leached per 100-g sample.

Calcining the concentrate at 700° C or increasing the leach temperature seems to increase the reaction rate only slightly, with a small, if any, decrease in the amount of MgO remaining in residue.

Acetic acid, sodium sulfite, and sodium sulfate were included to determine if the presence of other weak acids or salts might effect a faster or more complete dissolution of the dolomite. The use of acetic acid, sodium sulfite, and sodium sulfate does not appear to have any effect on either the dissolution rate or the final concentration of MgO in the residue. These results indicate that leaching sample 2, as received, with $170 \ 1b \ So_2$ per ton of concentrate will remove 0.32 to 0.40 pct MgO from the residue, regardless of all test variables. Grinding to minus 200 mesh slightly increased the amount of MgO leached.

The heads, calculated by adding the percent MgO leached to the residue analysis, averaged 1.07 pct MgO, in close agreement with the 1.15-pct-MgO analysis. Petrographic analysis had indicated 2.25 pct of type 1 dolomite, which amounts to 0.49 pct MgO and compares very well with the 0.32 to 0.52 pct leached shown in table 6.

SIMULATED COUNTERCURRENT LEACHING

A four-stage countercurrent leaching circuit was simulated using a series of four 600-mL beakers as leaching vessels. Solids were introduced and discharged from the leaching circuit by simply removing the beakers that had been through four leaching cycles at stage 1 and adding a fresh beaker at stage 4. The beaker containing 100 g of sample 3 concentrate and 100 mL of water, to simulate a 50-pct slurry, entered the circuit at stage 4.

The fresh lixiviant was charged to stage 1 as 300 mL of 2.9-pct SO₂. The lixiviant was transferred through the system by pouring 300 mL of solution into the next higher number stage; fresh solution was added to stage 1, and the spent lixiviant was discharged from stage 4. The beakers were moved forward one stage during the liquid transfer to preserve the countercurrent feature of the leaching circuit. Each cycle consisted of (1) a 15-min leach, (2) taking a 5-mL liquid sample for MgO analysis, (3) the addition of a fresh ore beaker, (4) the transfer of 300 mL of solution to the stages, in turn, and (5) the discharge of the finished beaker and spent lixiviant.

During startup, beaker 1 is subjected to four leach cycles with fresh acid, at 170 lb SO_2 per ton, before the circuit is filled with liquid and the normal progression started. Beaker 4 is the first beaker to go through a four-cycle progression through the leach cycle from which spent lixiviant is discharged. The solid-liquid transfer after the fourth cycle is shown schematically in figure 6; the process continued until nine beakers were used. After the lixiviant had contacted four beakers, it was removed from the circuit; after each ore sample had been leached four times it was removed from the circuit, and the residue was analyzed for MgO.

From the analysis of the leached residue and the four lixiviant samples, a material balance was calculated for each stage of the leaching process. The errors in the chemical analyses and sampling are cumulative, which leads to variation in the calculated heads and material balances for each individual stage, but conclusions can be drawn from the preponderance of the data.

The results show that in beaker 1 the solid MgO analysis drops the most during the first leach cycle and by lesser amounts during each successive leach. The residue from the fourth leach gave the lowest MgO of any of the residue samples.

After leaching has reached steady state, in about the fifth beaker, there is little dissolution of the MgO in stages 2, 3, and 4, with virtually all the MgO dissolution occurring in stage 1 with 170 lb SO_2 per ton of concentrate. The MgO leached during the four-stage leach was about 0.5 pct and was comparable to the MgO leached in beaker 1 after



FIGURE 6. - Schematic of countercurrent leach circuit.

the first leach. In other words, when leached with $170 \ 1b \ SO_2$ per ton of concentrate, it was immaterial whether the leaching was done in a single stage or in multistages of countercurrent leaching.

These results correlate with three forms of MgO observed in the petrographic

 SO_2 was effective in leaching part of the MgO from three phosphate concentrates. The flow rate of the SO_2 and the length of time leached were major factors in determining the amount of MgO leached. Calcining the samples prior to leaching and the use of high pulp densities during leaching gave modest improvements. Grinding the sample to minus 65 mesh did not improve leaching, but grinding to minus 200 mesh gave some

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4. Llewellyn, T. O., B. E. Davis, G. V. Sullivan, and J. P. Hansen. Beneficiation of High-Magnesium Phosphate From Southern Florida. BuMines RI 8609, 1982, 16 pp. analysis. The type 1 dolomite was readily leached by SO_2 . The type 2 phosphatized dolomite was not readily leached by countercurrent leaching with 170 lb SO_2 per ton, but was leached in beaker 1 by the four 170-lb- SO_2 -per-ton batches of fresh acid. The type 3 individual rhombs of dolomite suspended in the phosphate matrix were not leached in either leaching system and remained in the residue from beaker 1.

The sample 3 concentrate had an MgO analysis of 1.5 pct. The residue from beaker 8 in the countercurrent leach should contain only types 2 and 3. Its analysis of 1.0 pct MgO indicates about 0.5 pct type 1 dolomite. The residue from beaker 1, the four cycles of fresh acid leach, should contain only the type 3 dolomite and contains 0.6 pct MgO, indicating about 0.4 pct type 2 dolomite.

CONCLUSIONS

improvements, as did increasing the leach temperature.

Some of the MgO is so intimately associated with the phosphate mineral that it could not be removed by leaching prior to acidulation. This amount of MgO appears to be about 0.6 pct in sample 1, about 0.7 pct in sample 2, and 1.0 pct in sample 3. The calculated heads for the three samples averaged 1.4, 1.1, and 1.5 pct MgO, respectively.

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