

IN-SITU MINING OF PHOSPHATE ORES

Final Report

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ABSTRACT

Presently the mining of Florida phosphate requires the movement of over a 100-ton of materials (overburden, sand, clay) for every ton of phosphate concentrate recovered. Not only is this energy intensive, but it also causes significant stress on the environment. In 2003, the Department of Energy solicited ideas for innovative mining ideas that could significantly improve the efficiency of mining.

An award was made to the University of Florida Engineering Research Center to evaluate the in situ mining of phosphates using an aqueous CO₂ solution. Tests were carried out in a 15.2 cm (6-inch) diameter column, 1.83 meter (6 feet) long at pressures up to 117.2 kg/cm² (40 psi). Results to date demonstrate that initially the MgO is leached from the ore and then the phosphate. While the tests are continuing, so far they have not demonstrated P₂O₅ concentrations that are economically attractive.

INTRODUCTION

The Florida phosphate industry is the largest mining industry in Florida, typically mining over 30 million tons of phosphate rock. Most of the rock used to produce phosphate fertilizer, providing one of the three major essential crop nutrients. Most of the phosphate fertilizer is exported, mainly to China and India.

The industry is currently under numerous economic and environmental pressures and well could disappear in the next few years. While some of these pressures relate to the conversion of the phosphate rock to fertilizer, they are small compared to those involving the mining of the phosphate rock.

Mining of the phosphate rock requires the movement of several hundred millions tons of overburden and phosphate matrix and disturbance of several thousand acres of land each year. The overburden and matrix are removed by electrically driven draglines with up to 60 cubic meter buckets. Because of pit walls collapsing, generally wet pit conditions, and inability to precisely see the top or bottom of the matrix, only about 80% of the matrix is recovered.

In addition, the unmined phosphate deposits are at a deeper depth and contain significantly more impurities that require additional treatments to be useful. The most significant contaminant is dolomite, which is a mixture of calcium and magnesium carbonate.

The mined matrix is typically slurried with water and pumped to the beneficiation plant through several (up to 15) kilometers of pipeline. The pumped rock is very erosive and quickly wears the pipe. While the pipe is typically rotated (most of wear is on the bottom) every few months, it has a typical life of only 2 to 3 years.

At the beneficiation plant, the matrix is washed to remove the clay. This generates over 30 million tons of waste clay each year, which is stored as slurry in impounded areas. These waste clay ponds not only tie up the land (40% of that mined) but also a large quantity of water. They are also potentially environmental liabilities, as the storage dams can break (two occurrences in the last 10 years). Even after reclamation, the clay settling ponds have limited usefulness, as they will not support much weight. The waste clay also contains about 30% of the phosphate in the matrix.

Finally, the mining operations are moving further and further away from the fertilizer production facilities, increasing the transportation costs for the rock.

Overall, the mining/beneficiation/transportation process is very energy intensive, environmentally unfriendly and requires the use of large quantities of water. Electrical consumptions are typically 90-100 KWh per ton and are at least 20% of the total mining/beneficiation cost. It is the largest expense in the mining operation.

An ideal solution to the above problem would be to develop a mining process that would not require the movement of anything but the phosphate minerals, not generate any clay disposal ponds, and would generate a high purity soluble phosphate.

It is known that CO_2 in solution (carbonic acid) will dissolve both dolomite and phosphate rock.¹ In fact this occurs in nature as the CO_2 in the air goes into solution in the ground water and very slowly dissolves the limestone, dolomite and phosphate rock in the ground. The calcium and magnesium go into solution as the bicarbonates. While the reaction is relatively fast for dolomite, it is much slower for phosphate rock.

However, these reactions could be sped up significantly by increasing the CO_2 in solution. This can be achieved by contacting the leach water with pure CO_2 at the hydrostatic pressure of the formation (60-120 kg/cm^2 (20-40 psi) absolute). If CO_2 saturated water is contacted with the phosphate matrix, by introducing it through solution mining well complex, it will quickly solubilize the calcium and magnesium as the bicarbonates. Since a bottom layer of hard clay or solid limestone typically bound the phosphate matrix, the solution will be confined to the matrix zone. Once the solution is recovered from the ground, the calcium and magnesium can either be precipitated as the carbonates and the CO_2 recovered by heating the solution, or precipitated as the sulfates by the addition of sulfuric acid and the CO_2 recovered. Once the calcium and magnesium carbonates have been removed from the formation, the CO_2 saturated water will begin to dissolve the phosphate. While the concentration of phosphate will be quite low (<1%), it may increase by refortifying the solution with CO_2 and reinjecting it into the ground to dissolve additional phosphate. The solubilized calcium can also be precipitated by the addition of sulfuric acid at this step or later in the process at a higher concentration

Since the pH of the solution will be about 5, very little else will go into solution. When the matrix has been depleted, the solution mining area can be restored by simply injecting a small amount of caustic into the well field.

Once the phosphate solution reaches about 1%, it can be economically concentrated to greater than 5 % by using the reverse osmosis (RO) process. The use of RO has been demonstrated to work at the 500,000 gal/day scale under similar conditions in the ongoing clean up of the Piney Point phosphoric acid plant near Tampa, Florida.² Further concentration of the phosphate solution can then be accomplished in a phosphoric acid evaporator. The concentrated acid can then be used to produce the typical phosphate fertilizer products.

In 2003, the Department of Energy solicited ideas for innovative mining ideas that could significantly improve the efficiency of mining. An award was made to the University of Florida Engineering Research Center to evaluate the in-situ mining of phosphates using an aqueous CO_2 solution.

EXECUTIVE SUMMARY

The mining of phosphate ore typically involves the movement of over 100 tons of materials (stripping, matrix hauling, restoration) to obtain one tone of concentrated phosphate ore. Overall, the mining/beneficiation/transportation process is very energy intensive, environmentally unfriendly and requires the use of large quantities of water. Electrical consumptions are typically 90-100 KWh per ton and are at least 20% of the total mining/beneficiation cost. It is the largest expense in the mining operation.

This research involves the removal of the phosphate by in-situ leach with a CO₂ saturated solution. The CO₂ saturated solution (carbonic acid) will first dissolve the dolomite (calcium magnesium carbonates) by converting them to the more soluble bicarbonates. The solution then dissolves the various forms of calcium phosphate bearing minerals by converting calcium to calcium bicarbonate and the phosphate to phosphoric acid. The success of this approach is in part dependent on the ability to produce concentrations of phosphoric acid that can be economically concentrated to useful concentrations. In existing central Florida phosphoric acid plants, the acid is typically produced at 27% P₂O₅. If a solution can be produced in-situ that is at least 1% P₂O₅, it should be economic to concentrate it to 27% by a combination of reverse osmosis and evaporation techniques.

Four Samples of phosphate matrix (raw ore) were collected from two different mines operated by IMC and Cargill. These samples were characterized as to solids content, particle size distribution, overall chemical composition and chemical composition by particle size. Additionally, portions were subject to XRD analysis to determine the major mineral content. As expected, quartz, SiO₂, francolite, fluorapatite, and carbonate fluorapatite were all identified in the various samples. The size distribution was determined for the minus 150 mesh (clay) fractions. Average particle sizes of 15-30 microns were measured which is typical for this type of matrix.

An in-situ leach simulation system was built that consisted of a CO₂ cylinder, soda fountain carbonator, and a 1.83 m (6 ft) tall by 15.2 cm (6 inch) diameter column filled with phosphate matrix. While the system could be safely run at pressures up to 293 kg/cm² (100 psi), the tests were run in, 58.6-117.2 kg/cm² (20-40 psi) range, as this is the pressure that would be seen at the typical phosphate formation depths.

Two sets of leaching tests were conducted. Both demonstrated the relative ease in leaching out the magnesium and calcium carbonates. Both also demonstrated that phosphate could be solubilized but only at concentrations up to 100 ppm. Refortifying the leachate with CO₂ and recycling it through the column again did not significantly increase the P₂O₅ concentration.

An attempt to precipitate the calcium in the leachate and then refortify with CO₂ before recycling through the column was not successful for the first test since the phosphate had already been depleted in the matrix. Time had run out in the contract before a similar test could be run on the second test. This test will be conducted in 2005 and reported to the DOE when the results are known.

EXPERIMENTAL

Four samples of phosphate matrix were obtained from both Cargill and IMC Phosphates. The characterization of these ore samples is given in Tables 1-2.

Table 1-Matrix Solids Content

Material	Solid%
Cargill High MgO	79
Cargill Low MgO	80
IMC Low MgO	79
IMC High MgO	75

Table 2- Chemical and size analyses of four samples

Cargill High MgO

Screen size, mm	%Wt	MgO %	P ₂ O ₅ %	CaO %	Al ₂ O ₃ %	Fe ₂ O ₃ %
+19	3.25	3.14	3.14	14.22	0.19	0.37
-19+2	8.38	11.79	11.79	20.48	0.50	0.48
-2+1	3.56	14.86	14.86	23.58	0.40	0.60
-1+0.42	42.54	8.11	8.11	12.18	0.13	0.37
-0.42+0.1	26.44	7.18	7.18	10.92	0.15	0.32
-0.1	15.82	2.45	2.45	6.63	5.68	1.53
Feed	100	0.92	7.23	12.11	1.19	0.52
Calc.Feed	100.00	0.96	7.36	12.14	1.06	0.56

Cargill Low MgO

Screen size, mm	%Wt	MgO %	P ₂ O ₅ %	CaO %	Al ₂ O ₃ %	Fe ₂ O ₃ %
+19	3.29	0.11	17.29	26.37	0.72	0.20
-19+2	11.50	0.18	14.47	22.51	0.92	0.45
-2+1	7.26	0.17	15.39	23.70	0.80	0.50
-1+0.42	26.30	0.05	4.6	6.79	0.22	0.19
-0.42+0.1	29.36	0.05	4.38	6.50	0.24	0.20
-0.1	22.29	0.48	3.21	4.58	5.14	0.75
Feed	100	0.21	6.32	10.04	1.39	0.39
Calc.Feed	100.00	0.17	6.56	9.89	1.46	0.37

IMC Low MgO

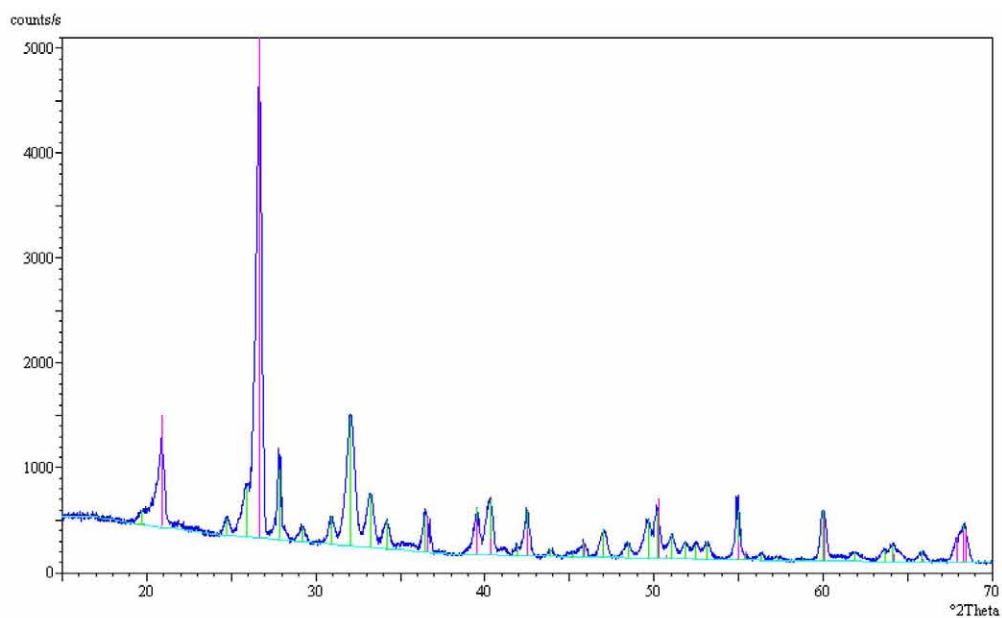
Screen size, mm	%Wt	MgO %	P ₂ O ₅ %	CaO %	Al ₂ O ₃ %	Fe ₂ O ₃ %
+19	1.09	0.25	14.27	22.53	0.46	1.36
-19+2	30.99	0.22	13.59	20.89	0.38	2.68
-2+1	17.23	0.17	13.8	21.01	0.45	5.47
-1+0.42	8.51	0.62	12.35	19.01	0.36	3.88
-0.42+0.1	12.53	0.13	9.64	14.75	0.5	1.89
-0.1	29.63	0.57	5.22	8.23	4.50	3.81
Feed	100	0.31	10.31	16.18	1.73	3.15
Calc.Feed	100	0.34	10.55	16.25	1.63	3.48

IMC High MgO

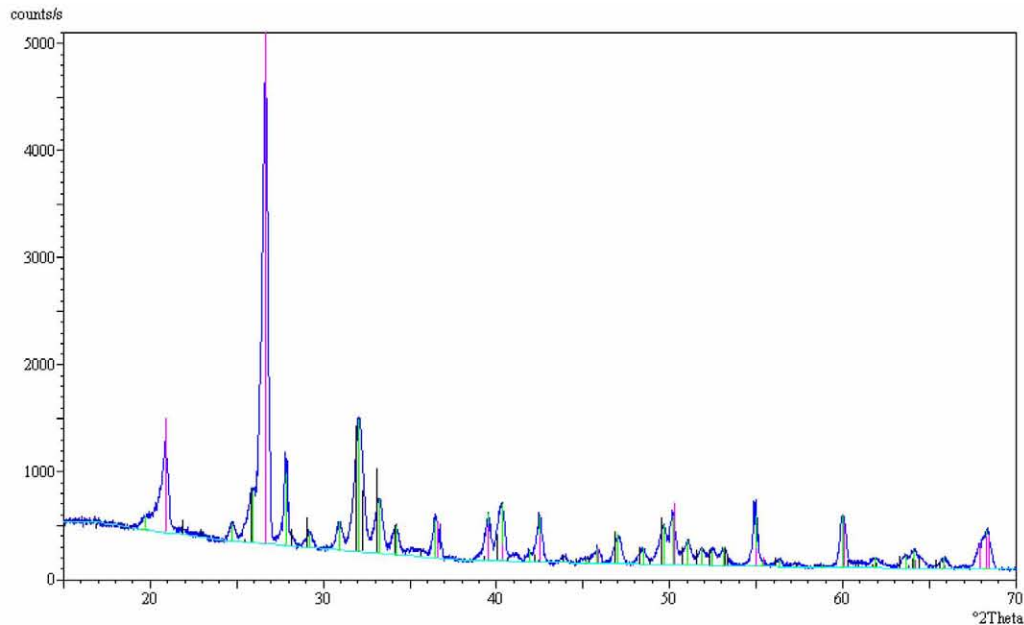
Screen size, mm	%Wt	MgO %	P ₂ O ₅ %	CaO %	Al ₂ O ₃ %	Fe ₂ O ₃ %
+19	0	0	0	0	0	0
-19+2	2.34	0.54	15.81	22.03	3.31	0.43
-2+1	2.12	0.32	15.17	20.70	3.08	0.42
-1+0.42	47.47	0.12	3.95	5.36	0.02	0.10
-0.42+0.1	34.55	0.04	2.86	3.78	0.34	0.20
-0.1	13.53	2.27	1.28	3.61	2.94	1.50
Feed	100	0.36	3.88	6.01	0.75	0.29
Calc.Feed	100	0.4	3.73	5.29	0.67	0.34

Samples of each matrix were subjected to Xray Diffraction studies with the following results:

Figure 1, XRD graphs for sample “Cargill low MgO”:

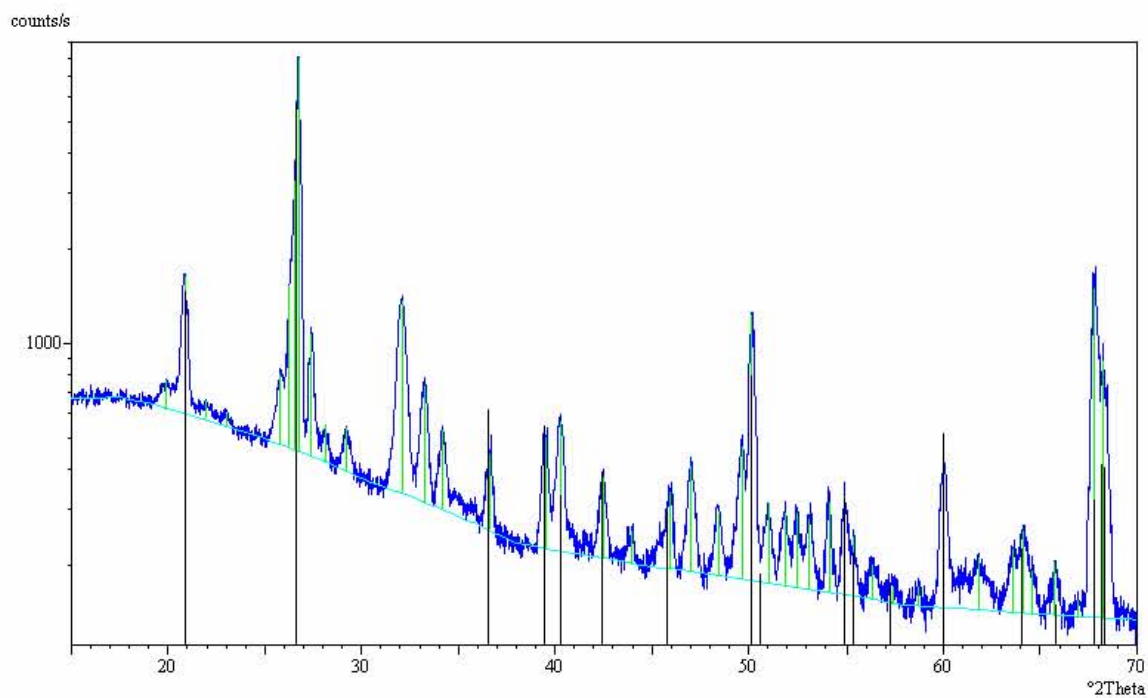


*The magenta lines correspond to Quartz, SiO₂, JCPDF 85-1054
Green lines: the peaks found by the software for the spectrum.*

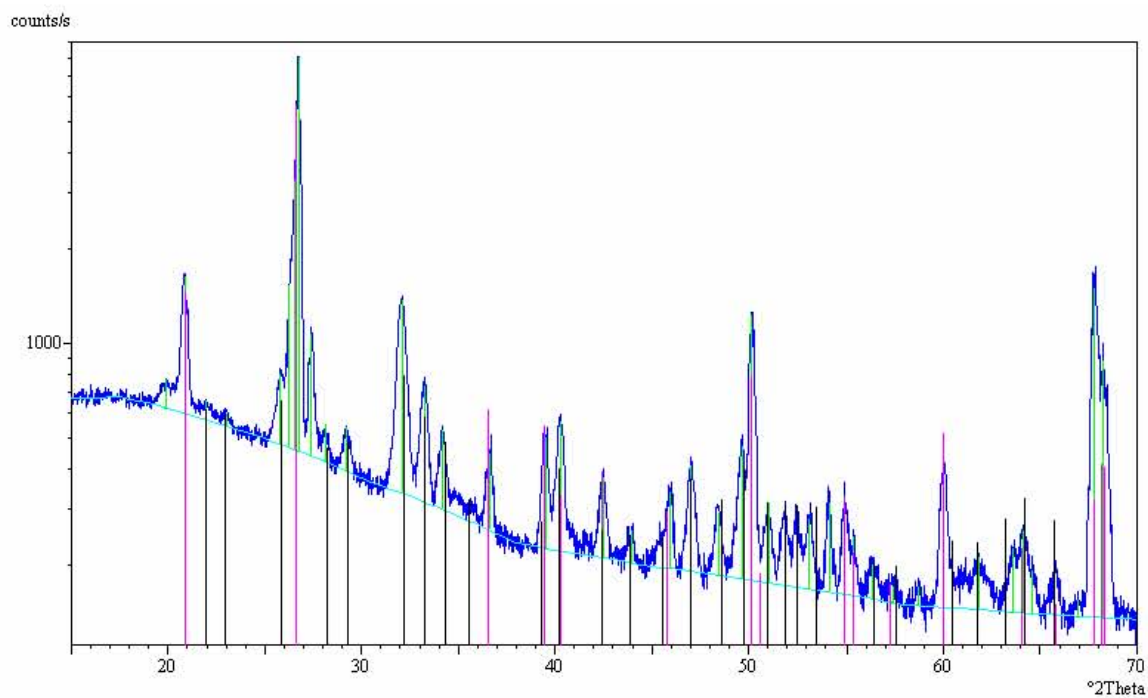


Magenta lines correspond to Quartz, black lines to Fluorite; there are several peaks (around 19, 24, 31 degs) that are not identified.

Figure 2, XRD graphs for sample “Cargill high MgO”:

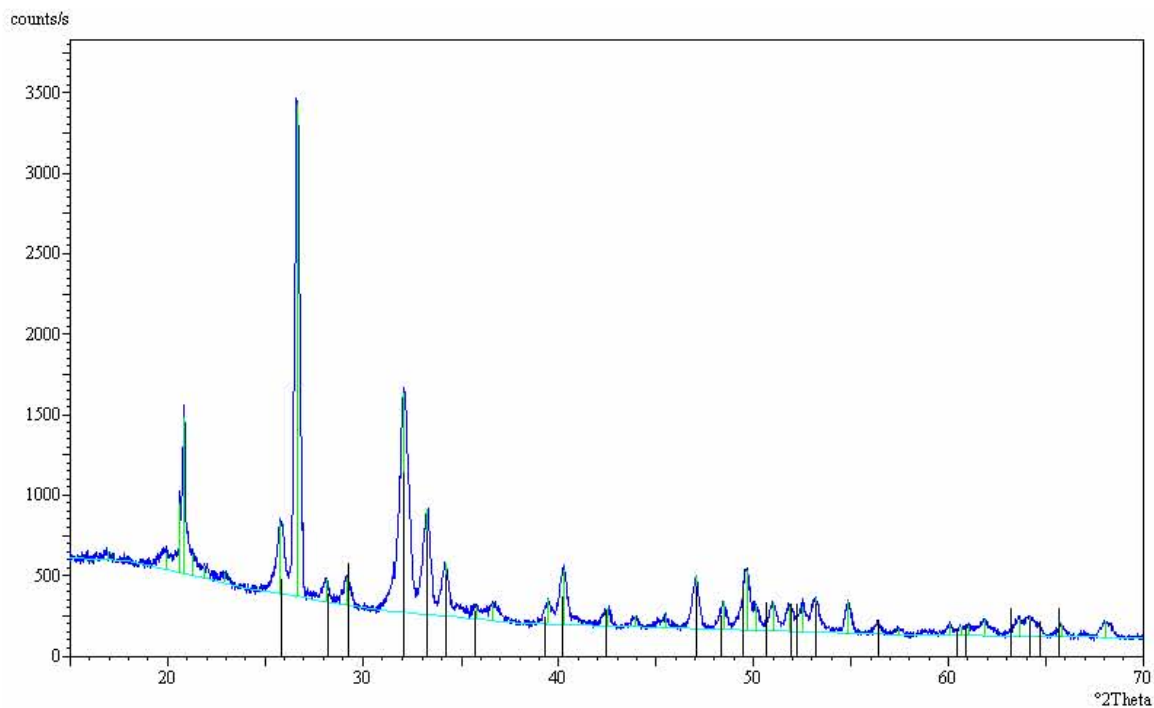


*Black lines correspond to Quartz;
Green lines are the peaks from the spectrum.*

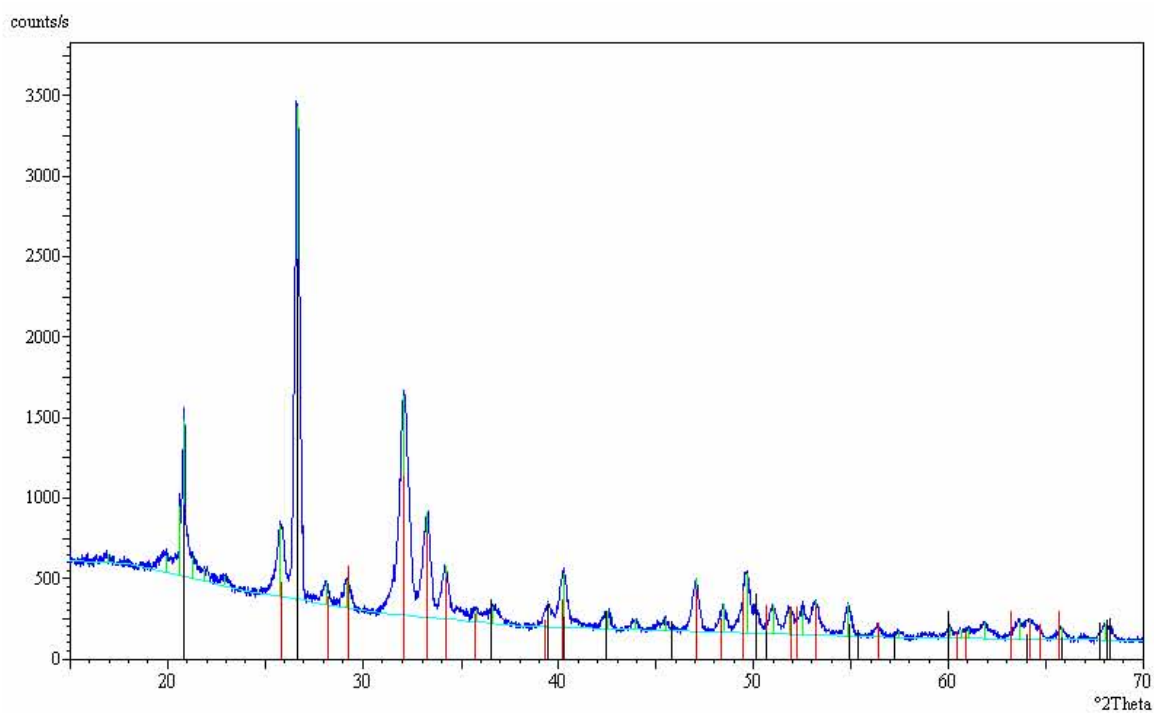


Black lines correspond to Fluorapatite, magenta lines Correspond to Quartz.

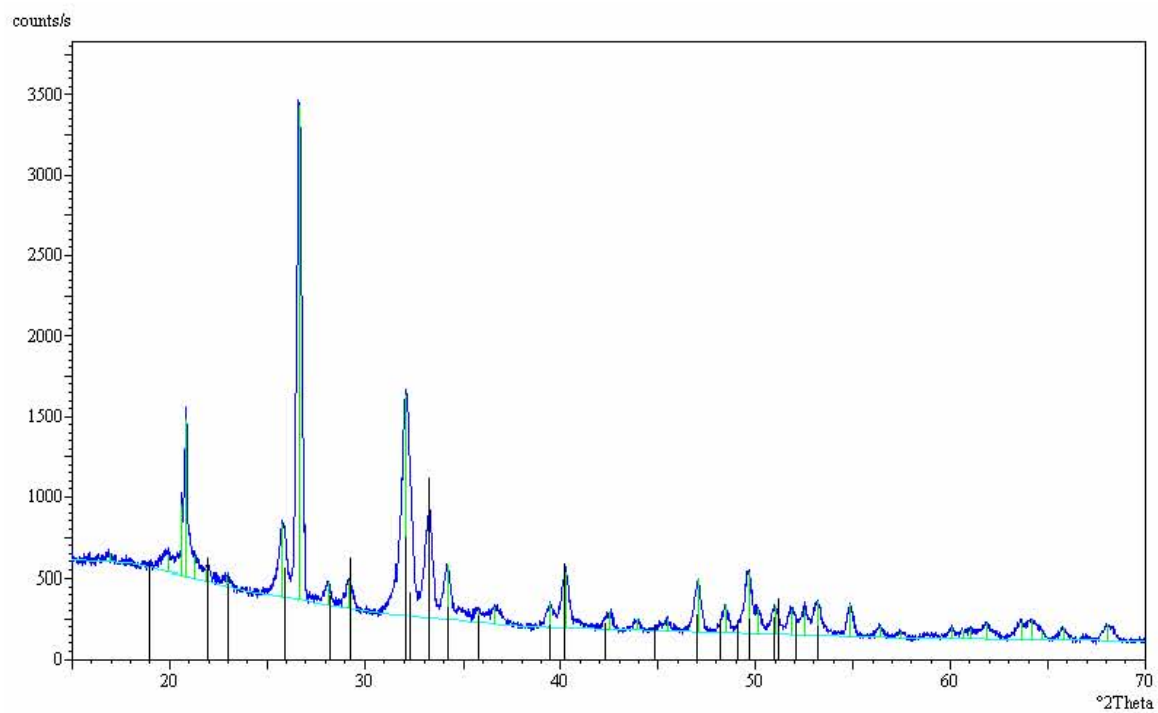
Figure 3, XRD graphs for sample “IMC low MgO”:



Black lines correspond to Francolite (02-0833).

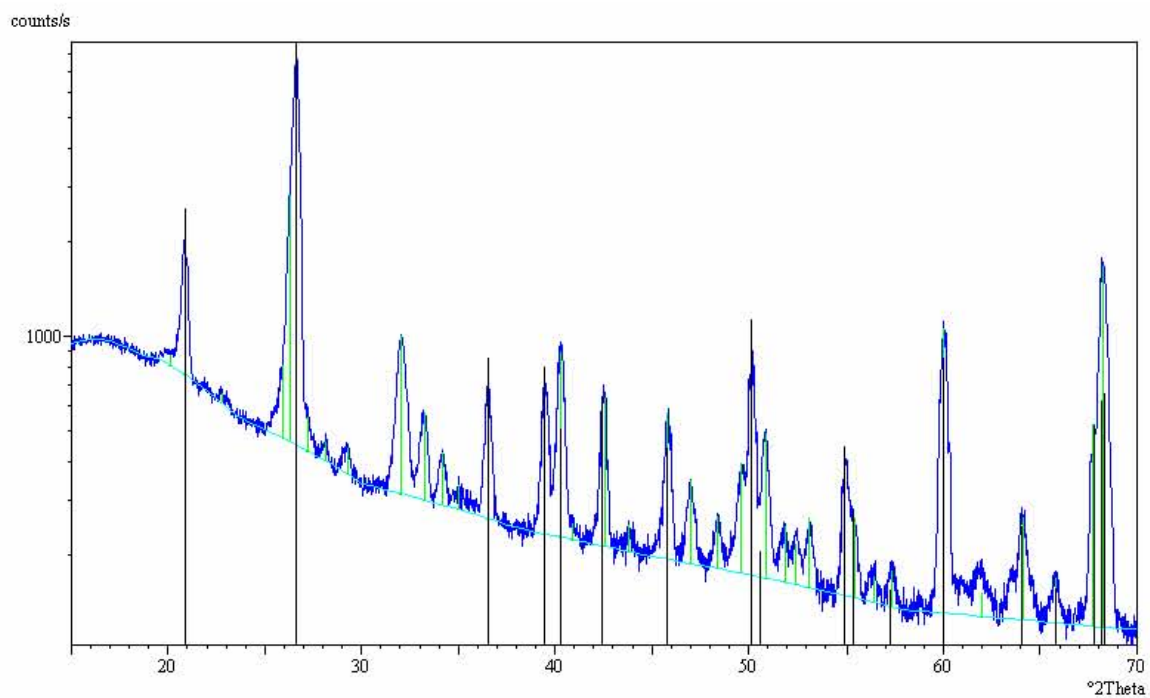


*Red lines correspond to Francolite; Black lines correspond to Quartz;
There are several small peaks that were not identified.*

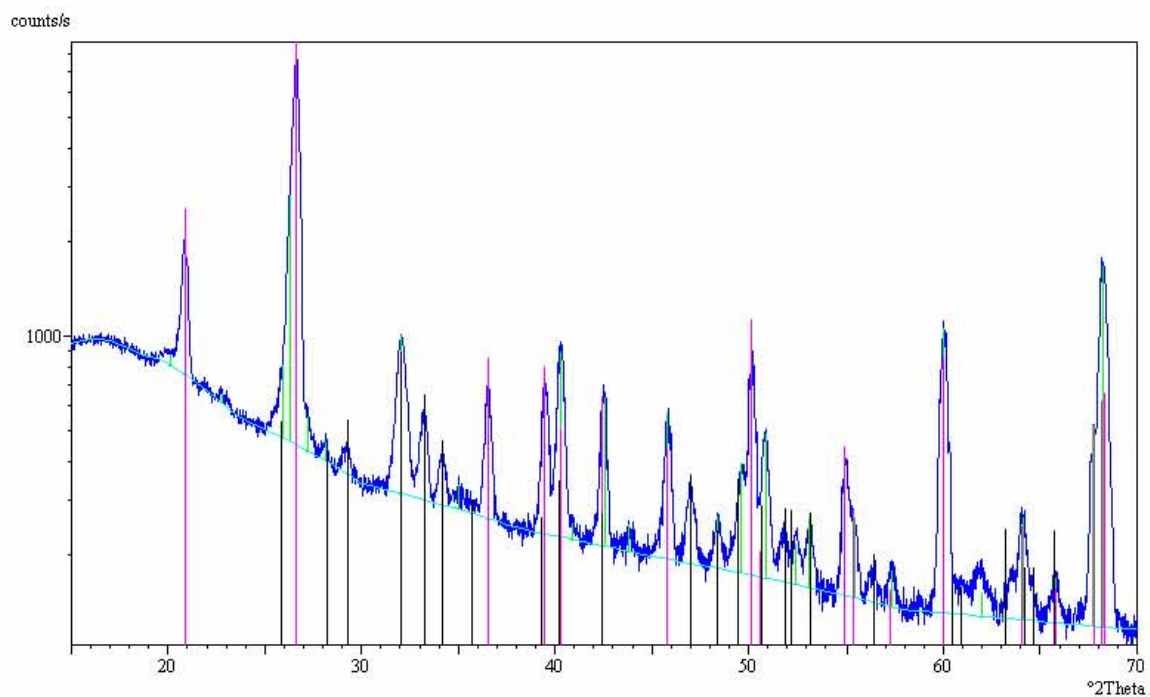


Black lines correspond to Carbonatefluorapatite(31-0267).

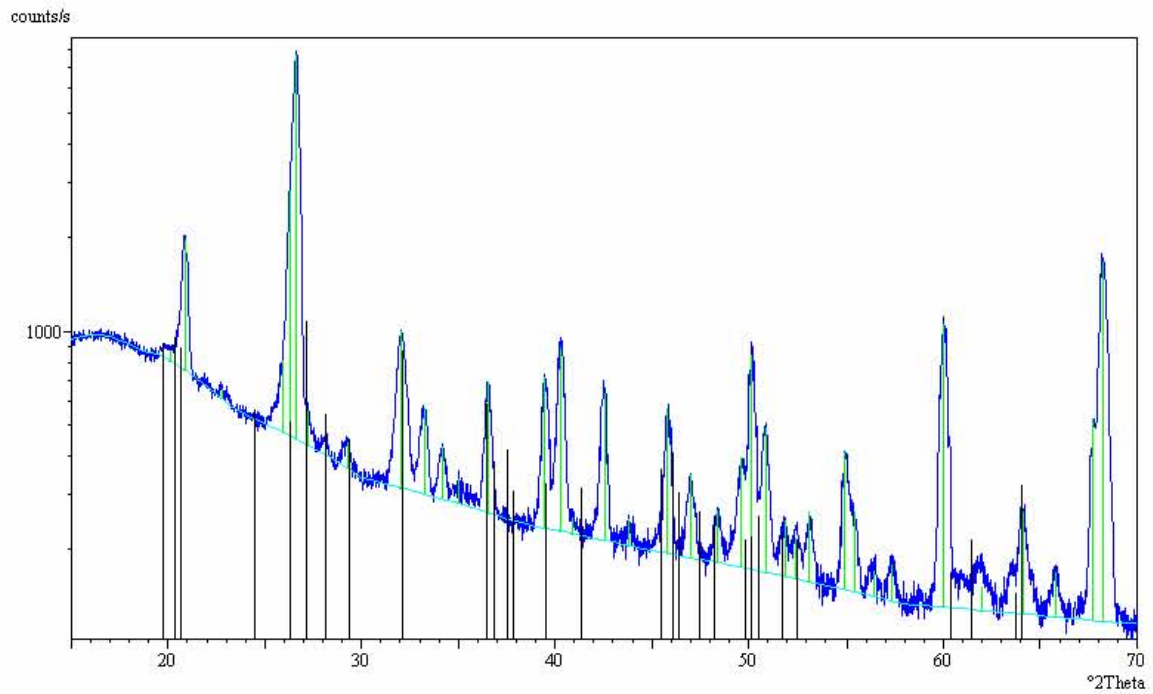
Figure 4, XRD graphs for sample “IMC high MgO”:



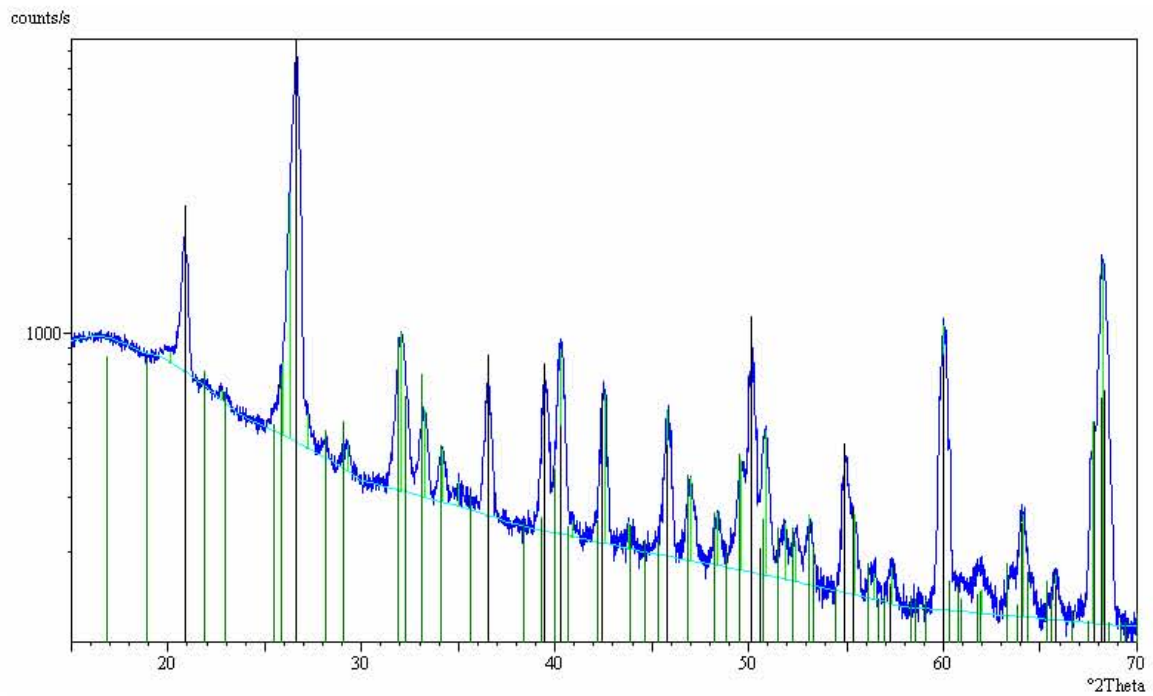
Black lines correspond to Quartz



Quartz + Francolite



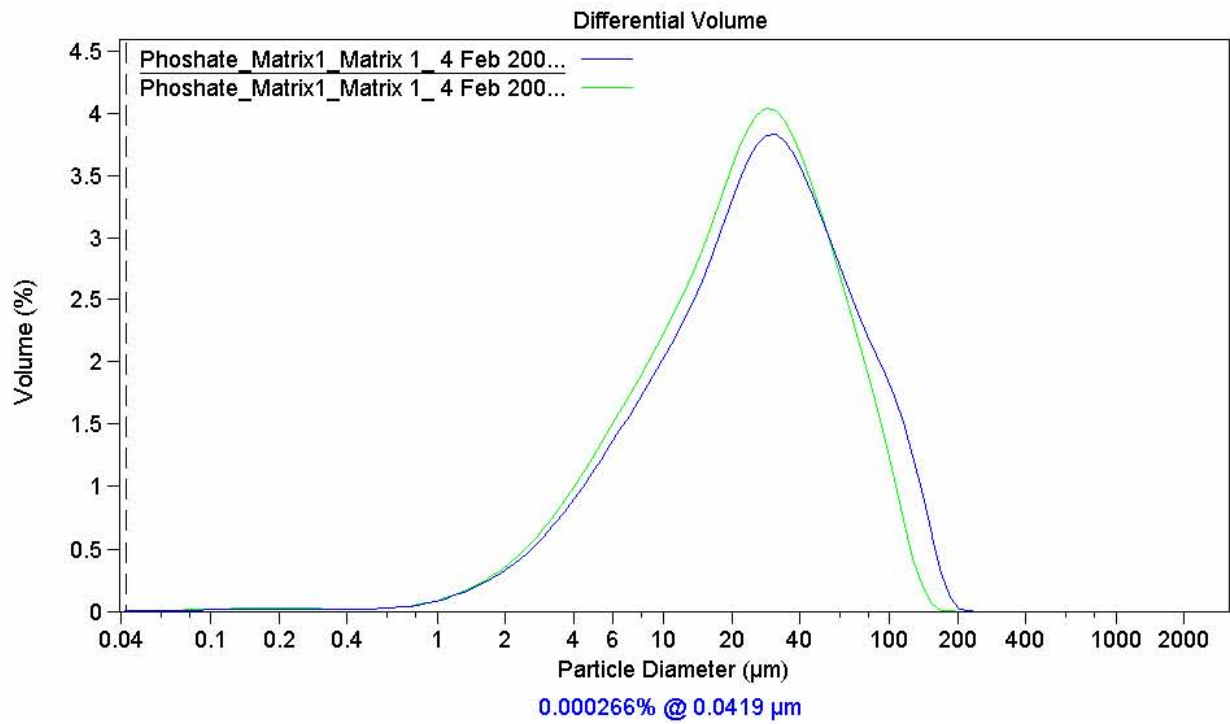
Black lines correspond to Aluminum Silicate, $\text{Al}_3\text{Si}_2\text{O}_7(\text{OH})_3$, JCPDF 49-00.



Quartz (black)+Fluorapatite (green).

The size distribution of the minus 150 mesh (clay) fraction was determined with the following results.

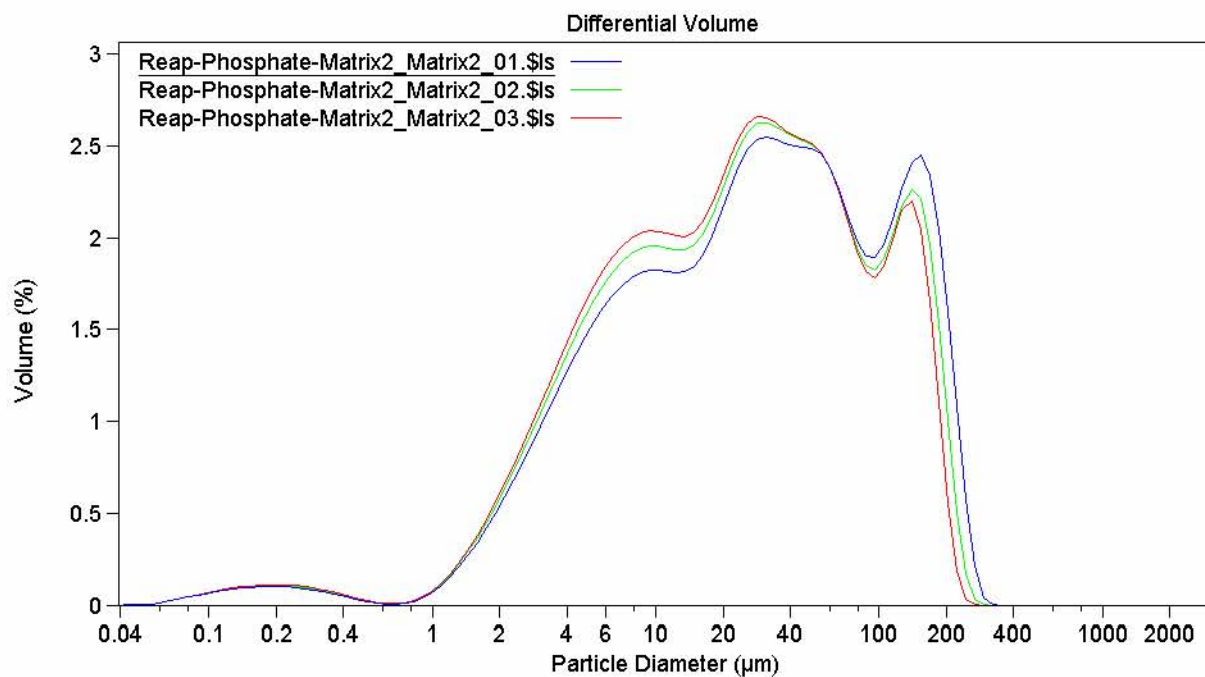
Figure 5, Size Distribution for (-150 mesh) of Cargill Low MgO:



Sample		Mean	S.D.	D50
* A S		23.3	2.90	26.3
	CML	20.5	2.79	23.6
	Average*	21.9	2.84	25.0

**Average of 2-measurements*

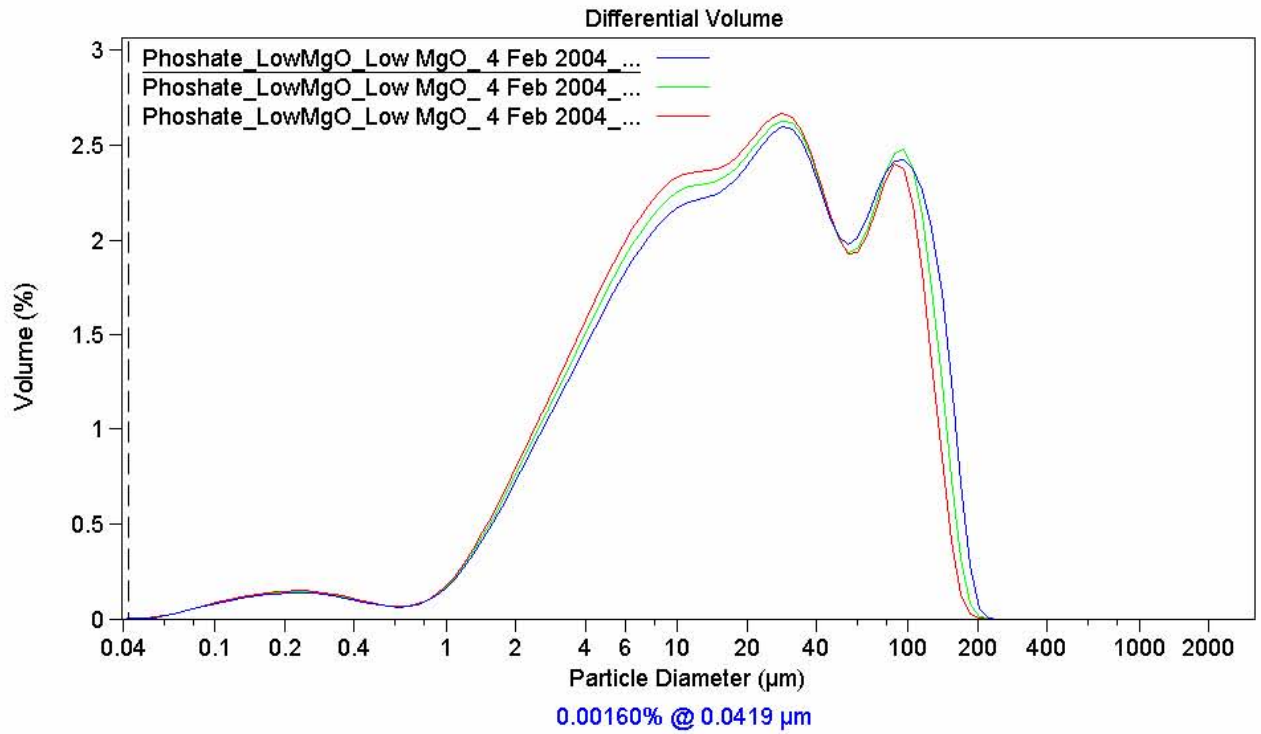
Figure 6, Size Distribution for (-150 mesh) of Cargill High MgO:



Sample	Mean	S.D.	D50
CMH	25.0	4.20	29.2
	22.4	4.08	26.1
	20.9	4.02	24.3
Average*	22.8	4.10	26.5

**Average of 3-measurements*

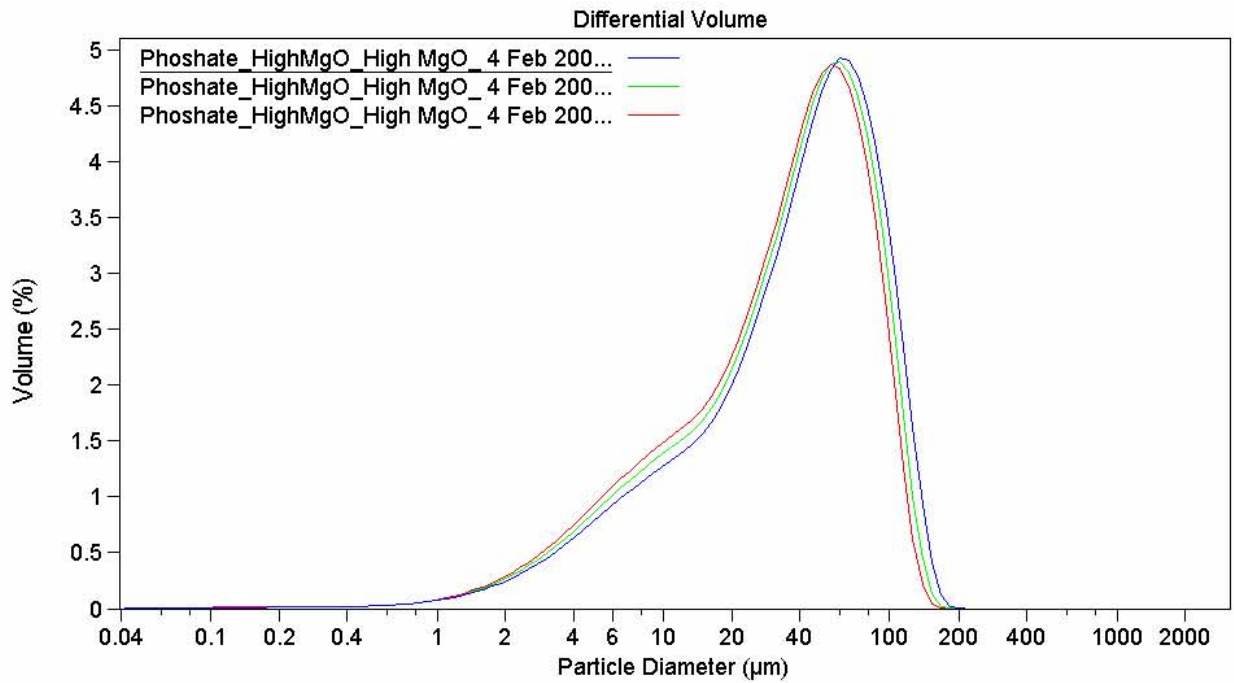
Figure 7, Size Distribution for (-150 mesh) of IMC low MgO:



Sample	Mean	S.D.	D50
IML	18.2	4.15	21
	17	4.08	19.5
	15.9	4.01	18.2
Average*	17	4.08	19.5

**Average of 3-measurements*

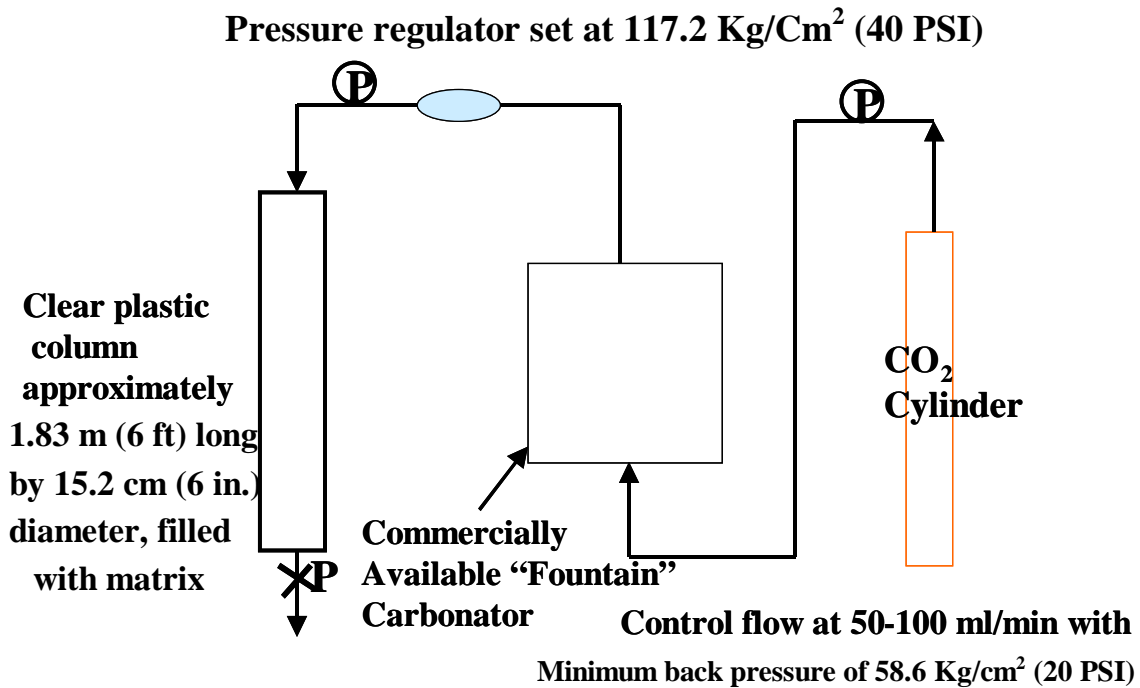
Figure 8, Size Distribution for (-150 mesh) of IMC high MgO:



Sample	Mean	S.D.	D50
IMH	32.9	2.84	42.9
	30.3	2.84	39.6
	28.3	2.85	37.1
Average*	30.5	2.85	39.9

A test system was built as shown in Figure 9.

Figure 9. Experimental Setup



The system consisted of a CO₂ Cylinder, a commercially available soda fountain carbonator, and a 15.2 cm (6-inch) diameter by 1.83 m (6 feet) long plastic column filled with matrix, several pressure gauges and a pressure regulator.

The column was initially packed with 45.15 kg (90.3 pounds) of the IMC high MgO matrix and a solution of deionized water saturated in CO₂ was fed in downflow at pressures up to 175.8 Kg/cm² (60 psi). However, the process of filling the column disturbed the clay fraction in the matrix and this plugged off the column in the first few hours reducing the flow to less than 20 ml/min. The feed was then changed to upflow and the feed rate controlled by adjusting the back pressure on the column.

Figures 10-12 show the quantity of Calcium, Magnesium and Phosphorous in the leachate vs. time.

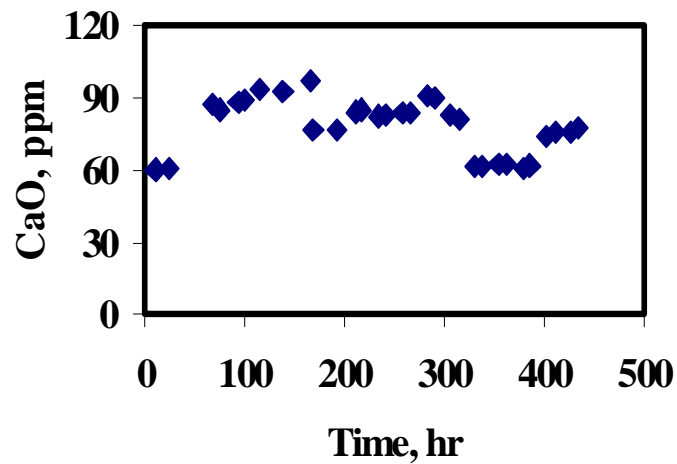


Figure 10. CaO in Leachate vs Time
 (50 ml/min, 58.6 Kg/cm² (20 psi) for first 265 hrs,
 150 ml/min, 117.2 Kg/cm² (40 psi) after)

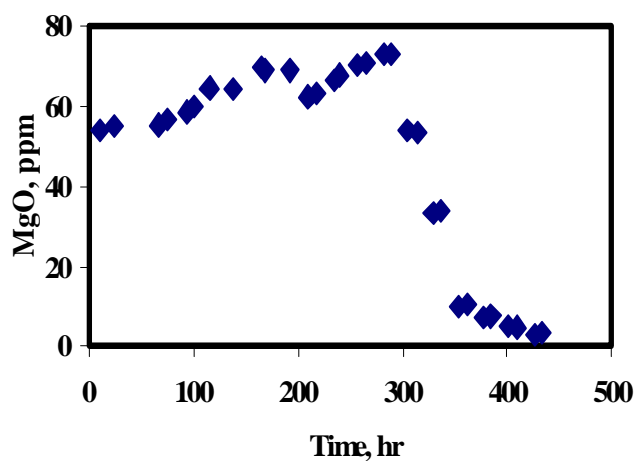


Figure 11. MgO in Leachate vs Time
 (50 ml/min, 58.6 Kg/cm² (20 psi) for first 265 hrs,
 150 ml/min, 117.2 Kg/cm² (40 psi) after)

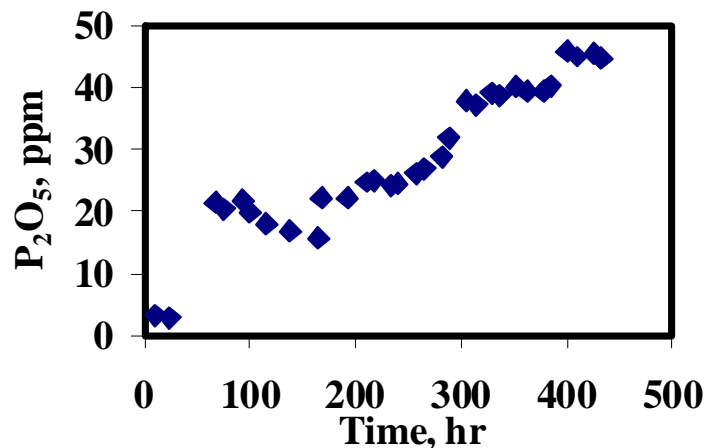


Figure 12. P₂O₅ in Leachate vs Time

(50 ml/min, 58.6 Kg/cm² (20 psi) for first 265 hrs,
150 ml/min, 117.2 Kg/cm² (40 psi) after)

As can be seen, after 300 hours, the MgO in the leachate began to drop and the P₂O₅ began to increase. This phase of the leaching was stopped after 433 hrs and the system modified to recycle the leachate after refortification with CO₂. Figures 13-15 show the results.

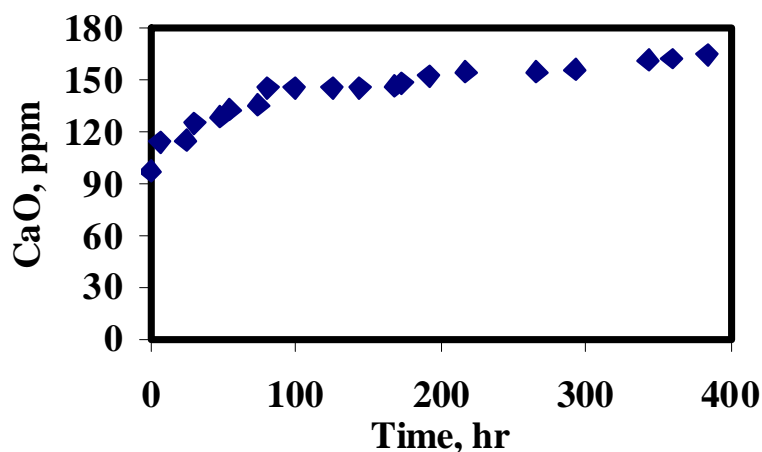


Figure 13. CaO in Leachate vs Time

Leachate Recycled at 150 ml/min after Refortification with CO₂ at 117.2 Kg/cm² (40 psi)

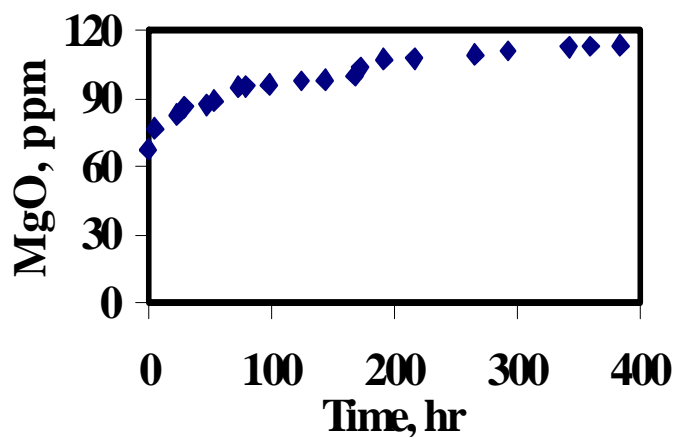


Figure 14. MgO in Leachate vs Time
Leachate Recycled at 150 ml/min after Refortification with CO₂ at 117.2 Kg/cm² (40 psi)

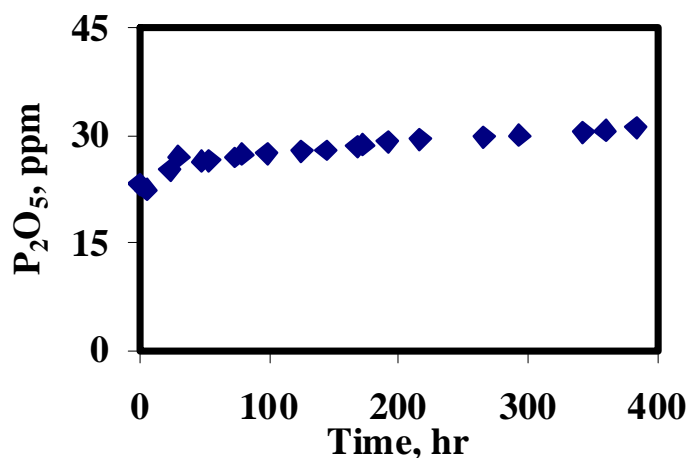


Figure 15. P₂O₅ in Leachate vs Time
Leachate Recycled at 150 ml/min after Refortification with CO₂ at 117.2 Kg/cm² (40 psi)

As can be seen, there was no significant increase in the P₂O₅ content of the leachate, indicating that the solution was at equilibrium with the matrix. At this point, an attempt was made to collect the leachate and precipitate the calcium before CO₂ refortification and recycling back to further increase the P₂O₅. However, a mass balance calculation showed that the matrix had been essentially depleted of P₂O₅.

The column was emptied and refilled with the IMC low MgO matrix. Figures 16 and 17 show the results for the first 264 hrs of leaching.

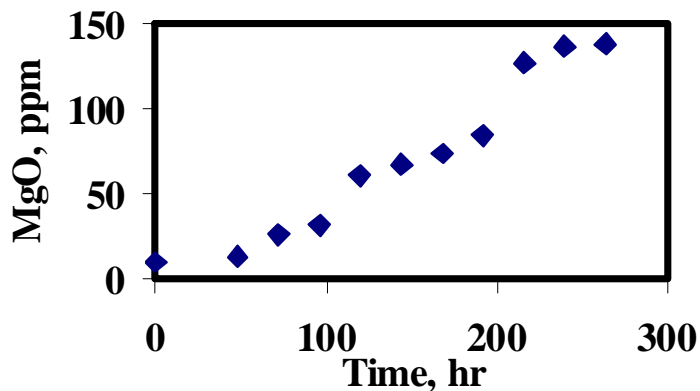


Figure 16. MgO in Leachate vs Time (55 ml/min, @ 117.2 Kg/cm² (40 psi) Feed Pressure)

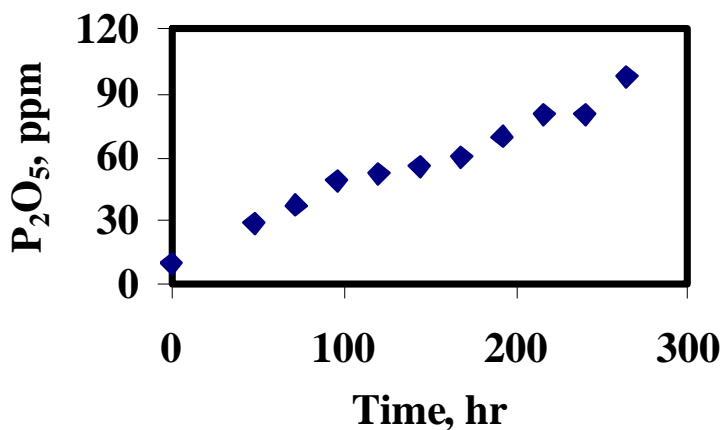


Figure 17. P₂O₅ in Leachate vs Time (55 ml/min, @ 117.2 Kg/cm² (40 psi) Feed Pressure)

At this point it was calculated that most of the MgO had been removed and the liquid was recirculated back through the column after CO₂ reformation. As in the first test, no significant increase in P₂O₅ content was observed. Presently, more than 400 liters of leachate has been collected and the calcium will be precipitated and the clarified leachate reformed with CO₂ in an attempt to increase the P₂O₅ content to the objective 1%.

If the P₂O₅ content of the leachate can be increased to 1% or above, it will then be concentrated to about 27% P₂O₅, and clarified. The clarified acid will then be analyzed for iron, aluminum, magnesium, and fluorine content to determine its compatibility with the current process for making high-grade phosphate fertilizers.

RESULTS AND DISCUSSION

The main objective of the test work was to determine if a P_2O_5 concentration of at least 1% could be achieved in the leachate from the matrix contained in the column. Time ran out before this could be demonstrated. (The experimental work on this program was significantly delayed when the initial post doc selected to perform the work was denied entry into the US from Egypt, and a second candidate had to be utilized.) While it is still hopeful that this will be achieved in tests that will be run in early 2005, we can not be certain that it will be achieved. When these results are known, the overall economics of the proposed process will be calculated and submitted as an additional report on the project.

CONCLUSIONS

1. Magnesium and Calcium can be removed from central Florida phosphate matrix using a CO_2 saturated solution.
2. Phosphate can also be removed from central Florida phosphate matrix using a CO_2 saturated solution.
3. Refortification of leachate with CO_2 and recycling it through the phosphate matrix does not significantly increase the phosphate concentration.

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