ABSTRACT

Many new phosphate mines yield rock phosphate in which there is a preponderance of magnesium, due to the presence of dolomite.

Existing fertilizer technology cannot tolerate magnesium in rock phosphate, above a certain specified limit. Thus it has become imperative that we have to resort to new technology, either for fertilizer manufacture or for demagnesifying the rock phosphate before further processing.

This paper presents the results of a new hydrometallurgical process for eliminating or bringing to specified limits the magnesium content of dolomitic rock phosphate. The process essentially consists of suspending pulverised rock phosphate in water and passing carbon dioxide gas through the slurry. It has been observed that under suitable conditions, the magnesium carbonate in the rock phosphate can be converted into the bicarbonate of magnesium. The magnesium bicarbonate thus formed passes into solution from which the demagnesified product may be separated. The product prepared thus has been analyzed using an X-ray Fluorescence Spectrophotometer and shows only traces of magnesium in it.

INTRODUCTION

Phosphate industry comprising mining, beneficiating and processing of naturally occurring deposits of calcium phosphate, is one of the major industries worldwide and particularly in the United States. The U.S. industry is located mainly in the central region of Florida where big deposits of land pebble phosphate were discovered over one hundred years ago.
Mining is done by electrically operated drag lines and the mined ore is beneficiated by high pressure waterwashing followed by flotation. Subsequently, it is pulverised and reacted with sulfuric acid to produce phosphoric acid. This acid is then converted to ammonium phosphates of various grades and granulated with or without the addition of muriate of potash.

Rock phosphate specifications include phosphate, calcium, magnesium, iron and aluminum. From the point of view of fertilizer the phosphate content is important. From the point of view of sulfuric acid consumption, the extra amounts of calcium as well as the iron and aluminum are critical. But of these latter components, magnesium is more important. Magnesium sulfate in the solution forms magnesium phosphate and forms compounds of a complex nature, unlike the iron and aluminum. These complexes impart a deleterious effect on the granulation of the final fertilizer slurry.

Florida deposits have been yielding rock phosphate of more or less uniform composition and these deposits have been calculated to last another 10 years or so (1). Already some areas in central Florida have started showing signs of exhaustion both in the quantity and in the quality of the ore. This has necessitated the exploration of new areas in the adjoining southern region towards which the deposits extend. However, the phosphate from this region is found to contain more magnesium than that allowed by specification. The magnesium content is mainly due to the presence of dolomite. A typical ore mined by a major producer is found to have the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt.%</th>
<th>Component</th>
<th>Wt.%</th>
<th>Component</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPL</td>
<td>62.73</td>
<td>P₂O₅</td>
<td>28.71</td>
<td>CaO</td>
<td>45.71</td>
</tr>
<tr>
<td>MgO</td>
<td>2.05</td>
<td>Fe₂O₃</td>
<td>0.90</td>
<td>Al₂O₃</td>
<td>1.11</td>
</tr>
<tr>
<td>F</td>
<td>3.25</td>
<td>SO₃</td>
<td>0.83</td>
<td>CO₂</td>
<td>6.42</td>
</tr>
</tbody>
</table>

The specification of magnesium in rock phosphate being 1.0% by weight (expressed as MgO), raw materials of the type in Table I cannot be processed in existing plants unless the rock is pretreated to bring the magnesium within specification. This problem had been recognized very early in regions where rock phosphate occurs only in the magnesium and calcium contaminated form. Much research has been and is being done to evolve an economic method to separate the extra magnesium and also the calcium from naturally occurring calcium phosphate. Most of the flotation work done towards this separation has resulted in the separation of silica only, because of the little selectivity between the phosphate and dolomite or calcite. Of late, with a better understanding of surface phenomena and the
availability of newer and more efficient chemicals, success with the flotation process looms in
the horizon more than ever before (2,3). Chemical methods, hydrometallurgical methods and
electrostatic methods and acid leach methods have also been developed with fair amounts of
success in the laboratory (4,5,6,7). In extreme cases of necessity, even the costly way of
calcination and air separation of the burnt lime and magnesia have been resorted to.
However, a suitable economic process to remove magnesia from dolomitic rock phosphate does
not seem to have been evolved yet. This paper presents the results of a series of experiments
carried out on dolomitic rock phosphate with a view to develop an economic process which
can result in the production of rock phosphate containing magnesium within the specified limit

PRINCIPLE

When magnesium carbonate (or oxide or hydroxide) is suspended in water and carbon
dioxide passed into the suspension, the carbonate is converted to the bicarbonate. This
bicarbonate of magnesium is soluble in water and remains dissolved as long as the
temperature of the solution is not raised above the ambient temperature or as long as further
calcium or magnesium salts are not added to the solution or as long as its pH is not altered.
The solubility of magnesium carbonate in water is very low at any temperature (in the 3rd.
decimal place only) (10), whereas, an 1.5% solution of magnesium bicarbonate is quite
possible to be made at room temperature by the above method (11). Increase of pressure or
decrease of temperature can give solutions of higher concentrations. In the following
experiments, only the room temperature and atmospheric pressure conditions were employed.
Calcium bicarbonate was also formed along with the magnesium bicarbonate, but the solubility
of the former is so markedly lower than that of magnesium bicarbonate that its effect, though
beneficial, may be neglected for all practical purposes, unless a very large quantity of water is
used. It is also found that other components or rock phosphate have no chemical action on
carbonic acid. On the basis of these, this study employing carbonic acid to leach out the
magnesium carbonate from dolomitic rock phosphate was conducted.

APPARATUS

The apparatus consisted of a glass vessel of 500 ml. capacity which had a fritted glass
bottom. The space below the fritted glass was connected to the vertical stem of an inverted Y
tube. All the three limbs of this Y tube carried glass stoppers. One of the lower limbs was
connected to a cylinder of compressed carbon dioxide gas. The other limb was connected to a Buchner flask which in turn was connected to a vacuum pump. This arrangement had the following advantages:

Stirring the reaction slurry by externally fitted stirrer was avoided since the bubbling of gas itself did the work of stirring.

* The fritted glass bottom could be made to act not only as the gas dispersant medium but also as a filter medium by closing the carbon dioxide valve and opening the valve leading to the Buchner funnel and the vacuum pump. The filtrate collects in the flask while the filter cake is caught on the fritted glass bottom of the vessel. After withdrawal of samples for analysis, the filtrate could be poured back to the vessel and the experiment continued.

MATERIALS

Two samples of rock phosphate were used in this series of experiments. Sample A analysed 2.05% by weight of MgO. This sample was procured from a mine in an area adjoining the south of central Florida region. Sample B contained 0.23% by weight of MgO and was from a working central Florida mine. Carbon dioxide gas used was from commercially available cylinders.

EXPERIMENTS

The samples were pulverised to minus 85 mesh size, the usual size of rock phosphate powder employed in the phosphoric acid plants.

In one experiment, 250 gm. of powdered sample A was taken in the glass vessel and to this, 350 ml. distilled water was added. Immediately the stopper on the vertical stem was opened and then the valve leading to the gas cylinder was slowly opened. Gas was admitted at the rate of half a liter per minute. After 15 minutes of reaction, the gas valve was closed and then the valve leading to the filter flask was opened. The vacuum pump was switched on. In about 20 seconds, the entire liquid from the vessel filtered into the Buchner flask. At this point, the valves on the vertical stem of the Y tube and that leading to the Buchner flask were closed successively. Half a gram of the filter cake sample was taken for analysis and the filtrate was then poured into the vessel. The reaction was then continued as before for another 15 minutes. At the end of this time, one more sample of the reacted powder was collected following the procedure mentioned above. The reaction was again carried on for another half an hour after which, one more sample of the reacted powder was collected.
FIGURE 1. X-RAY FLUORESCENCE SPECTROGRAPH OF UNTREATED APATITE (SAMPLE A)

FIGURE II X-RAY FLUORESCENCE SPECTROGRAPH OF APATITE (SAMPLE A) AFTER 15 MINUTES LEACHING WITH CARBONIC ACID.
The three samples collected from the different stages of the reaction as well as a sample of the untreated rock phosphate were analysed for magnesium using an X-ray Fluorescence Spectrophotometer. The filtrate was treated with a slurry of calcium hydroxide to a pH of...
9.5 and the precipitated carbonates of magnesium and calcium were filtered and dried and analyzed. The results are presented in Figures I to V.

The same sequence of operations were repeated, using sample B. The results are presented in Figures VI to IX.

**DISCUSSION OF RESULTS**

Figure I is the analysis of sample A as such. The heights of the peaks indicate the relative abundance of the various elements in the sample. It may be noted that the height of the magnesium peak is almost twice as high as that for alumina as is to be expected from the analysis given in TABLE 1.

In figure II which represents the analysis of the sample after 15 minutes of reaction with carbonic acid, it may be seen that the magnesium peak has been reduced appreciably indicating that a corresponding amount of magnesium has been leached out.

In Figure III further leaching is shown to have taken place during the next 15 minutes. The amount of magnesium has reached almost the same level as of alumina.

Figure IV shows that magnesium carbonate in the sample has been almost completely leached out. The magnesium peak is hardly discernable. To verify this information, the
Figure V is the spectrogram of the mixed carbonates of magnesium and calcium precipitated from the leached liquor. This shows the presence of significant amounts of magnesium, extracted evidently from the rock phosphate only.

Figure VI and Figure VIII are the spectrographs of sample B, before and after leaching for half an hour. Magnesium is very low in the sample itself so that both the spectrographs
had to be magnified as before to observe the change in magnesium content brought about by the leaching. The magnified spectrographs of Figures VI and VIII are shown in Figures VII and IX respectively. It may be clearly seen that whatever magnesium that was present in the sample B had been leached out as indicated by the absence of a peak for magnesium in Figure IX.

The above experiments conclusively prove that dolomitic rock phosphate can be demagnesified by carbonic acid leaching under proper conditions.

CONCLUSIONS

Magnesium carbonate bearing rock phosphate will pose processing problems to the phosphatic fertilizer industry in the very near future. The work presented in this paper has demonstrated that practically all of the magnesium carbonate in the rock can be leached under ordinary pressure and temperature conditions. Carbon dioxide is a relatively cheap commodity especially since it is present in the flue gases of coal burning burners and boilers. Because of this easy availability, the process may be expected to be economically viable also.

It may be noted that since all of the magnesium may be removed by this method, it is only necessary to treat an aliquot part of the mined material. The treated magnesium-free portion may then be mixed with the untreated portion so that the mixture will have magnesium within the specified limit. Finally, the suggestion may be ventured that since the Indian Mussoorie rock phosphate as well as that from the Lakhdive Islands contain large amounts of calcium and magnesium, this method may be tried on them hopefully.

ACKNOWLEDGEMENTS

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REFERENCES


5. U.S. Patents 3,022,890 and 3,063,561


