BY-PRODUCT GYPSUM IN ILLINOIS — A NEW RESOURCE?

H. P. Ehrlinger III, B. F. Bohor, and G. C. Finger
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ABSTRACT

Over 11 million tons of waste gypsum (calcium sulfate) has accumulated at seven sites in Illinois. Waste gypsum is the crude, insoluble, filter cake by-product from the wet-process manufacture of phosphoric acid, the basic ingredient of phosphate fertilizers. One site also receives a small amount of waste gypsum from a hydrofluoric acid plant.

Samples were collected from each site for a detailed study of the gypsum's properties to determine whether it might be a useful new mineral resource. Acidity (pH) tests and chemical analyses of the major, minor, and trace constituents were made, and photomicrographs were taken of the crystal form. Resulting data are compared with similar information for natural rock gypsum and wallboard. A location map, aerial photographs, and tonnage estimates are included in the report. By-product gypsum possibly could be used in wallboard, stucco, and cement, as a source of sulfur or sulfuric acid, as a filler in paints, plastics, and textiles, and as a soil conditioner and stabilizer.

INTRODUCTION

With the rapid depletion of many of our prime mineral resources, our industrial economy is being forced into mining and processing lower-grade resources. The many mine dumps and tailings, industrial chemical waste piles, and urban refuse heaps all across the nation are now being considered as possible secondary mineral sources. An added incentive to their use is the fairly recent public awareness of their pollution potential and their unsightliness on the landscape.
To implement the search for possible secondary mineral sources, the Illinois State Geological Survey is reporting the whereabouts and suggesting possible uses of mine refuse piles, spoil banks, overburden backfills, and by-product accumulations from industrial minerals operations in the state. Industrial Minerals Note 36, for instance, discussed recovery of kaolinite from silica sand washings.

This report is concerned with by-product gypsum, a calcium sulfate waste generated in large tonnages during the chemical processing of natural rock phosphate to phosphate fertilizer, detergents, or other products. Anhydrite (CaSO$_4$), the completely dehydrated form of gypsum, is a by-product in the production of hydrofluoric acid from fluorspar (CaF$_2$) (Bradbury, Finger, and Major, 1968).

The formula for natural rock gypsum is CaSO$_4$·2H$_2$O, but waste gypsum varies widely in its water of composition and in the amount of impurities it contains. Heating at 128°C (262°F) converts gypsum to hemihydrate (CaSO$_4$·½H$_2$O). Further heating at 163°C (325°F) converts it to anhydrite.

Waste gypsum has been considered substandard in the past for the conventional structural uses of gypsum, such as wallboard. Reasons for its rejection are its acidity, crystal nature, moisture content, inconsistent coefficient of expansion, and the bleeding through of impurities during and following painting.

GYPSUM WASTE PILES IN ILLINOIS

Seven major storage piles of by-product gypsum in Illinois (fig. 1) were sampled for this study.
The owners of these piles were most helpful during our investigation, and we are grateful for their assistance. The sample numbers used in this report, the companies involved, and the location of the piles follow.

1. Blockson Works, Olin Corporation, Joliet
2. Northern Petrochemical Corporation (Norchem), Morris
3. National Phosphate Corporation, Beker Industries, Marseilles
4. New Jersey Zinc Company, Depue
5. Smith-Douglass Chemical Division, Borden, Incorporated, Streator
6. U.S. Industrial Chemicals Company (U.S.I.), Tuscola
7. Allied Chemical Corporation (Allied), East St. Louis

The gypsum in these piles is the by-product formed during the extraction of the phosphate from rock phosphate by the so-called wet process. Because of its source, this gypsum is also known as phosphogypsum or phosphatic gypsum. The Olin Corporation pile at Joliet also contains anhydrite from a hydrofluoric acid plant.

The wet process involves the digestion of finely ground rock phosphate, which when pure is expressed Ca$_3$(PO$_4$)$_2$, with sulfuric acid. A phosphoric acid solution and a calcium sulfate precipitate are formed, as illustrated by the equation

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4 \downarrow$$

When the reaction slurry is filtered, the gypsum precipitate forms a filter cake, which is reslurried for washing and discharged to the storage pile.

Most rock phosphate, sometimes expressed as Ca$_{10}$(PO$_4$)$_6$F$_2$, contains about 3 percent fluorine and a variety of minor trace impurities, such as iron, silica, titanium, and uranium. Some impurities are removed by solution during the wet process, and only a relatively small amount remains in the gypsum residue. In the refining of the crude phosphoric acid solution, the fluorine is recovered as a valuable by-product and provides the chemical industry with a large fluorine reserve. The uranium, as the oxide U$_3$O$_8$, can also be recovered from the phosphate liquor, as was done in 1954 at the Olin plant.

The gypsum slurry is discharged into holding ponds for dewatering and storage. The ponds are surrounded by a dike, or berm, 15 to 25 feet high. The Smith-Douglass plant at Streator deposits its gypsum waste below ground level in pits once quarried for clay. The decanted water is generally reused in the plant.

The known deposits of wet-process, by-product gypsum in Illinois are at the plant locations shown in figure 1 (Harre, 1969). Detailed locations are given in table 1, and the aerial photographs in figure 2 show the nature of the storage piles. Over 11.5 million tons of this by-product, which has a composition (CaSO$_4$·N$_2$H$_2$O), approximating that of mineral gypsum, is stock-piled at these Illinois locations.

Most of the rock phosphate used in Illinois comes from extensive deposits in Florida and is transported to Illinois by way of the Gulf of Mexico.
and the Mississippi River. Most of the wet-process acid plants, therefore, are located on or near the Mississippi or Illinois Rivers. The U.S.I. plant at Tuscola, Douglas County, however, could not be supplied via water, and its rock phosphate was shipped in by rail from Florida deposits.

**TEST SAMPLES**

Samples of waste gypsum weighing more than 25 pounds each were taken from at least two areas of the four piles visited (locations 1, 2, 3, and 4, table 1). One sample generally was taken from the berm, or dike, material that formed the holding pond and another was taken from the pond itself.

Smith-Douglass at Streator sent us a filter cake sample, and U.S.I. at Tuscola and Allied at East St. Louis sent composite samples from their current waste production and their waste storage ponds.

**CHEMICAL ANALYSES FOR MAJOR, MINOR, AND TRACE ELEMENTS**

Prior to chemical analysis and solubility tests, the gypsum samples were oven dried at 93° C (200° F) for 24 hours. They were then pulverized and passed through a 200-mesh screen.
Major elements in the samples were determined by X-ray fluorescence, with the exception of sulfur, which was analyzed by the conventional gravimetric (wet chemical) method. Minor and trace elements were determined by optical emission and/or neutron activation analysis. All chemical analyses in this report were made by the Analytical Chemistry Section of the Illinois State Geological Survey.

Neutron activation analysis was especially useful in the detection of trace elements. Uranium (U) and lanthanum (La) were detected and measured at the 3 parts per million (ppm) level. Bromine, iodine, gold, silver, copper, arsenic, antimony, cobalt, gallium, indium, scandium, europium, hafnium, tantalum, tungsten, and platinum were not detected in amounts greater than 100 ppm.

The chemical analyses of the seven waste gypsum deposits and a commercial wallboard are given in table 2. Considerable variations appear in the amounts of major elements in the deposits, and significant differences are evident even in different samples from the same deposit. The variations in the amounts of trace elements present are not considered significant. In general, the data indicate that the method of processing, age, variation in phosphate feedstock, and degree of leaching are the most significant factors in the composition of the by-product gypsum.

Because the amounts of phosphorus (\(P_2O_5\)), fluorine (F), silica (SiO\(_2\)), iron (Fe\(_2O_3\)), and trace elements are higher in waste gypsum than in natural gypsum, the end use of the by-product material is strongly restricted by these impurities. Its higher acidity also must be considered in planning its ultimate use.

PHOTOMICROGRAPH ANALYSES

Most of the samples were studied with a polarizing microscope. The raw, dried samples were sprinkled into an immersion liquid (glycerine) on a glass slide. All photographs were taken with Pantatomic-X film in polarized light at a magnification of 10X.

The photomicrographs (fig. 3) illustrate the texture and morphology of the samples. For comparison, photomicrographs of natural rock gypsum and commercial wallboard gypsum are included in the figure.

In general, the waste gyspums are composed of subspherical, radially overgrown aggregates with some varieties of either cruciform or single euhedral (rhombic) crystals (table 3). The National Phosphate sample (fig. 3C) contains more single rhombs than the others. The New Jersey Zinc sample (fig. 3D) displays the only radically different morphology, being composed of large, zoned, and foliated overgrown crystals, with minor amounts of the usual radially overgrown aggregates. The Norchem sample (fig. 3E) contains fine, subspherical aggregates, and the Olin, U.S.I., Smith-Douglass, and Allied samples appear to be quite similar. The commercial wallboard sample (fig. 3B) is composed of fine
LOCATION 1
A. BLOCKSON WORKS, OLIN CORPORATION, near Joliet, new pond. Currently in use.

LOCATION 2
B. NORTHERN PETROCHEMICAL CORPORATION (formerly Des Plaines Chemical Company) pond near Morris. Not currently being filled.

LOCATION 3
C. NATIONAL PHOSPHATE CORPORATION, BEKER INDUSTRIES, pond near Marseilles. Currently in use.

LOCATION 4
D. NEW JERSEY ZINC COMPANY pond near Depue. Not currently being filled.
LOCATION 5
E. SMITH-DOUGLASS CHEMICAL DIVISION, BORDEN, INCORPORATED impound area near Streator. Old clay pit being used for storage. Currently in use.

LOCATION 6
F. U.S. INDUSTRIAL CHEMICALS COMPANY pond near Tuscola. Not currently being filled.

LOCATION 7
G. ALLIED CHEMICAL CORPORATION pond near East St. Louis. Currently in use.

Fig. 2 - Aerial views (A through G) of by-product gypsum storage.
### TABLE 2—CHEMICAL ANALYSES OF BY-PRODUCT GYPSUM AND WALLBOARD

<table>
<thead>
<tr>
<th>Site no., company, and sample location</th>
<th>Major elements (%)</th>
<th>Loss on ignition (%)</th>
<th>Minor or trace elements (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>SO₃</td>
<td>P₂O₅</td>
</tr>
<tr>
<td>1. Blockson</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Old pond - center</td>
<td>37.23</td>
<td>33.84</td>
<td>0.99</td>
</tr>
<tr>
<td>Old pond - berm</td>
<td>36.59</td>
<td>26.51</td>
<td>0.91</td>
</tr>
<tr>
<td>New pond - center</td>
<td>37.44</td>
<td>30.25</td>
<td>1.03</td>
</tr>
<tr>
<td>New pond - berm</td>
<td>37.91</td>
<td>31.23</td>
<td>0.72</td>
</tr>
<tr>
<td>2. Norchem (inoperative)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pond - center</td>
<td>34.55</td>
<td>36.11</td>
<td>0.67</td>
</tr>
<tr>
<td>Pond - berm</td>
<td>34.73</td>
<td>43.92</td>
<td>0.70</td>
</tr>
<tr>
<td>3. National Phosphate Corp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inner pit</td>
<td>32.50</td>
<td>42.37</td>
<td>0.96</td>
</tr>
<tr>
<td>Outer berm</td>
<td>34.60</td>
<td>46.80</td>
<td>1.20</td>
</tr>
<tr>
<td>4. New Jersey Zinc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inner pit</td>
<td>31.50</td>
<td>39.47</td>
<td>1.35</td>
</tr>
<tr>
<td>Outer berm</td>
<td>35.60</td>
<td>46.53</td>
<td>1.35</td>
</tr>
<tr>
<td>5. Smith-Douglass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composite sample</td>
<td>38.60</td>
<td>51.19</td>
<td>1.13</td>
</tr>
<tr>
<td>6. U.S.I. (inoperative)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composite sample</td>
<td>33.20</td>
<td>42.88</td>
<td>1.01</td>
</tr>
<tr>
<td>7. Allied</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composite sample*</td>
<td>40.41</td>
<td>54.29</td>
<td>0.51</td>
</tr>
<tr>
<td>8. Commercial wallboard</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composite sample</td>
<td>32.50</td>
<td>38.43</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* Al₂O₃ = 0.57  n.a. = no analysis  n.d. = not detected
A. Rock gypsum from Shoals, Ind.

B. Commercial wallboard

C. From National Phosphate Corp. storage pond

D. From New Jersey Zinc Co. storage pond

E. From Norchem storage pond

Fig. 3 - Photomicrographs showing crystal variations of natural and by-product gypsum.
<table>
<thead>
<tr>
<th>Site no., company, and sample location</th>
<th>CaO (%)</th>
<th>SO₂ (%)</th>
<th>P₂O₅ (%)</th>
<th>F (ppm)</th>
<th>pH</th>
<th>Fig. no.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Northeen northeen</td>
<td>0.28</td>
<td>0.45</td>
<td>0.01</td>
<td>18</td>
<td>5.2</td>
<td>3E</td>
<td>&quot;Ghost&quot; aggregates—indicative of leaching by meteoric (rain) water.</td>
</tr>
<tr>
<td>Old pond - center</td>
<td>0.28</td>
<td>0.48</td>
<td>0.02</td>
<td>13</td>
<td>5.0</td>
<td></td>
<td>Radially overgrown aggregates and individual smaller crystals of anhedral shape.</td>
</tr>
<tr>
<td>Old pond - berm</td>
<td>0.24</td>
<td>0.41</td>
<td>0.02</td>
<td>18</td>
<td>4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New pond - center</td>
<td>0.26</td>
<td>0.45</td>
<td>0.03</td>
<td>26</td>
<td>4.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New pond - berm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Norchem (inoperative)</td>
<td>0.28</td>
<td>0.48</td>
<td>0.02</td>
<td>27</td>
<td>4.8</td>
<td>3E</td>
<td>Large, spherical, radially overgrown aggregates (correlate with granular, free-flowing, bulk characteristics).</td>
</tr>
<tr>
<td>Pond - center</td>
<td>0.24</td>
<td>0.41</td>
<td>0.02</td>
<td>25</td>
<td>4.7</td>
<td>3E</td>
<td></td>
</tr>
<tr>
<td>Pond - berm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. National Phosphate Corp.</td>
<td>0.28</td>
<td>0.49</td>
<td>0.02</td>
<td>18</td>
<td>4.8</td>
<td>3C</td>
<td>Small rhombic crystals and irregular aggregates.</td>
</tr>
<tr>
<td>Inner pit</td>
<td>0.29</td>
<td>0.49</td>
<td>0.02</td>
<td>26</td>
<td>4.9</td>
<td>3C</td>
<td></td>
</tr>
<tr>
<td>Outer berm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. New Jersey Zinc</td>
<td>0.29</td>
<td>0.48</td>
<td>0.10</td>
<td>17</td>
<td>4.5</td>
<td>3D</td>
<td>Large, radially overgrown aggregate crystals and large, foliate, zoned or layered crystals.</td>
</tr>
<tr>
<td>Inner pit</td>
<td>0.28</td>
<td>0.45</td>
<td>0.16</td>
<td>19</td>
<td>3.3</td>
<td>3D</td>
<td></td>
</tr>
<tr>
<td>Outer berm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Smith-Douglass</td>
<td>0.30</td>
<td>0.44</td>
<td>0.07</td>
<td>29</td>
<td>3.6</td>
<td></td>
<td>Spherical, radially overgrown aggregate crystals; cruciform crystals; single euhedral crystals.</td>
</tr>
<tr>
<td>Filter cake sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. U.S.I. (inoperative)</td>
<td>0.28</td>
<td>0.49</td>
<td>0.04</td>
<td>19</td>
<td>4.6</td>
<td></td>
<td>Spherical aggregates with crystal dust.</td>
</tr>
<tr>
<td>Composite plant sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Allied</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
<td>Spherical, radially overgrown aggregates; dust; cruciform crystals; rare single euhedral crystals.</td>
</tr>
<tr>
<td>Composite plant sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Natural rock gypsum</td>
<td>0.23</td>
<td>0.50</td>
<td>&lt;0.01</td>
<td>0.42</td>
<td>6.1</td>
<td>3A</td>
<td>Large, rhombic, single crystals; smaller crystal fragments; dust.</td>
</tr>
<tr>
<td>Shoals, Ind.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Commercial wallboard</td>
<td>0.23</td>
<td>0.40</td>
<td>&lt;0.01</td>
<td>1.2</td>
<td>6.2</td>
<td>3B</td>
<td>Mostly spherical aggregates with some dust.</td>
</tr>
<tr>
<td>n.a. = no analysis.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
powdery aggregates with no definite structure. The rock gypsum (fig. 3A) is composed entirely of rhombic crystals and cleavage fragments.

SOLUBILITY AND ACIDITY TESTS

Because examination of the samples under the polarizing microscope showed crystal forms differing from those of natural gypsum, qualitative solubility tests were made for comparison with natural gypsum. The solubility procedure involved adding 300 cc of distilled water to 100 g of gypsum and agitating the slurry for 48 hours at room temperature. After the slurry had settled, a 100 cc portion of clear supernatant liquid (leachate) was removed by pipette and its pH determined. The liquid sample was then diluted with an equal volume (100 cc) of distilled water and analyzed for calcium (CaO), sulfur (SO₄), phosphorus (P₂O₅), and fluorine (F).

Table 3 summarizes the data on solubility, pH, and crystal structure. The solubilities of natural, waste, and wallboard gypsum were much alike in terms of their percentages of CaO and SO₄, even though higher solubility might be expected in the wallboard because of its fine grains. It appears that a reasonable saturation level was reached. X-ray diffraction analysis confirmed that some of the waste gypsum had been converted to anhydrite and hemihydrate forms. Processes used in the plant from which the waste gypsum came could have produced the anhydrite, whereas laboratory drying could account for the hemihydrate.

The waste gypsum, which had a pH ranging from 3.3 to 5.2, was more acidic than the natural gypsum, which had a pH of 6.1. The low phosphorus and fluorine values indicate that those impurities were in relatively insoluble form in the original by-product.

POSSIBLE USES OF WASTE GYPSUM

Building Materials

Gypsum in this country is used mainly for building materials—wallboard, cement, and plaster. By-product gypsum has never been used for these purposes because of its impurities. The impurities, principally phosphorus and fluorine, impart undesirable properties to the gypsum wallboard. For instance, they may cause paint on the wallboard to blotch, and if the phosphorus content (based on P₂O₅) is not well below one percent the wallboard may be weak. Setting time during manufacture also would be slow. A third impurity, aluminum in the form of AlF₅⁻², may cause the hemihydrate form of gypsum to be insensitive to retarders, making it useless for making plaster (Kitchen and Skinner, 1971).

As shown in table 2, the percentages of phosphate, fluoride, and aluminum (Al₂O₃) in the by-product gypsums from the Illinois deposits exceed greatly the values reported for commercial wallboard. However, the Giulini
process (Ellwood, 1969) of reducing these impurities to acceptable levels is attracting commercial interest. This patented German process converts, by recrystallization in an autoclave, by-product gypsum into alpha-hemihydrate gypsum, which is stronger than the beta form commonly obtained by calcination. Impurities from the phosphate rock are decreased during the recrystallization. Crystal growth can also be controlled during autoclaving to produce larger crystals that would provide increased strength in the final structural product.

Recently developed processes for manufacturing phosphoric acid (Chem. Week, 1971) form hemihydrate instead of gypsum as a by-product. The hemihydrate can be reslurried and hydrated to the dihydrate (gypsum). These processes yield a filter cake of gypsum containing only 0.2 to 0.8 percent phosphate, which meets the specifications for wallboard and plaster of good quality. Some such process should be considered for any new phosphoric acid plants or plant modernizations. British patent 1,202,893 (Fisons Fertilizers, Ltd., 1970), concerning the use of hemihydrate for plaster compositions and plaster board, may encourage use of such waste.

A slurry of gypsum stucco is sprayed on the structural steel of many buildings as a fire-retardant layer. If the stucco is to be hidden from view and no paint is to be applied, impure by-product gypsum may successfully compete with the natural material.

Natural gypsum, and possibly phosphogypsum, can be used as a substitute for clay in making insulating bricks and in place of portland cement as an anhydrite binder in heavy concretes, particularly those used in radiation shielding (Eipeltauer, 1958).

Cement

Natural gypsum is commonly used in the manufacture of portland cement. The gypsum acts as a strengthening and set-retarding agent when added to the cement clinker in amounts between 3 and 6 percent (Budnikov, Azelitskaya, and Lokot, 1968). Cement plants that use calcium sulfate instead of calcium carbonate are being designed by various engineering firms (Chem. Week, 1968; Remirez, 1968; Chem. Eng. News, 1968). In general, the gypsum is mixed with sand, coal or coke, clay or shale or fly ash, and sometimes pyrite or other sources of iron oxide. The entire mixture is roasted in a rotary kiln at about 1200° C (2192° F); the gypsum reacts with the constituents to form the mixture of calcium silicates and aluminates that characterize portland cement. Sulfur dioxide (SO₂) is driven off in the process and can be directed to a sulfuric acid plant. By-product gypsum can be used in the process if the final phosphate content in the cement clinker is between 0.1 and 1.8 percent. Thus two useful products are obtained from a by-product, and pollution problems are alleviated.

In general, by-product gypsum has not been preferred for cement manufacture because of the supposedly adverse influence of its high percentages of phosphate and fluoride on cement quality (Ind. Minerals, 1970). However, some workers (Kim and Lee, 1968) found no significant difference in the final setting times or strengths between cements using natural and by-product gypsum as a retarder additive as long as the sulfate contents were equal. As the gypsum
from the Illinois storage piles has rather low phosphate and fluoride percentages, it merits serious consideration for direct use, without purification, in cement clinker manufacture.

**Sulfur and Sulfuric Acid Recovery**

As indicated previously, processes have been developed for the recovery of sulfur from natural and by-product gypsum, with sulfuric acid and cement clinker as the end products (Chem. Eng. News, 1968). A Texas chemical plant that was designed to make elemental sulfur from gypsum was unable to achieve full operational status because of economic conditions (Chem. Week, 1968). These processes are not competitive with low-cost Frasch sulfur, by-product sulfur from petroleum refining, and projected stack-gas sulfur. However, in South Africa a chemical company has recently put into operation possibly the first plant in the world to produce sulfuric acid and cement from waste gypsum. The gypsum is a by-product of a phosphoric acid operation (Oil, Paint and Drug Reporter, 1973).

**Fertilizers, Soil Conditioners, and Stabilizers**

Ammonium sulfate fertilizer can be produced from natural gypsum or phosphogypsum by the Merseberg process (Ind. Minerals, 1970) developed in Germany between 1914 and 1918. The process involves the reaction of gypsum with an ammonium carbonate solution to give ammonium sulfate in solution and a calcium carbonate precipitate. Both the ammonium sulfate and the calcium carbonate, when mixed with ammonium nitrate, can be sold as fertilizer, or the calcium carbonate can be used alone for agricultural lime or in cement manufacturing. Several plants in India are using this process.

Gypsum is useful as a soil additive for agricultural purposes. Over 9 percent (1 million tons) of the total annual production of gypsum in the United States is used for soil treatment, mainly to neutralize the alkaline soils of the west, especially in California (Aldrich and Schoonover, 1951). An estimated 100,000 tons of ground anhydrite per year is used in the southeastern states to promote the growth of peanuts (Appleyard, 1970). Agricultural bulletins from peanut-growing states indicate this use is nearer 250,000 tons per year.

In Illinois and surrounding states, highly alkaline soils are not common, but patches and streaks of soil with a high sodium content occur occasionally with the more productive soils (Fehrenbacher et al., 1966). These alkaline soils, also called "clay slicks," delay cultivation in the spring because they dry slowly. In addition, they do not hold moisture adequately during dry periods because they crust and crack easily. Yields in such alkaline areas are considerably lower than those from surrounding soils. One way to improve these high-sodium soils is to mix them with gypsum. The calcium ion in the gypsum replaces the sodium ion on the clay particles in the soil and thereby improves its moisture retention, water percolation, and tilth (Padhi et al., 1965). Tests described in the literature are not conclusive, but they seem to indicate that yields improve if the gypsum is well mixed into the soil and is applied generously (Fehrenbacher et al., 1967).

A recent newspaper article (Champaign-Urbana News-Gazette, 1971) reports the use of phosphogypsum from the U.S.I. waste gypsum deposit at Tuscola
for counteracting the salt content in soil that had been polluted by oil wells in the area. Dead leaves also were applied to supply humus and to control erosion.

In addition to neutralizing alkali-rich soils, gypsum is used to increase the calcium-to-magnesium ratio on agricultural land that has an excessive magnesium content. The optimum ratio will vary with the crop, but 4:1 is common. Many soils in the Midwest have or develop a high magnesium content. By-product phosphogypsum is being used to correct that condition in several midwestern states. Phosphogypsum, which often costs less than the pure agricultural limestone usually used for this purpose, contains beneficial trace elements and the additional plant-nutritive values of the phosphorus.

Gypsum has been studied as a soil stabilizing agent, but the results generally have been unsatisfactory, according to several unpublished reports. Calcined limestone (lime) is much more reactive in soils and provides a high degree of stabilization.

Miscellaneous Uses

Waste gypsum also could be used as a filler in some paints, plastics, and textiles, as an ingredient in glass, as a filter for water treatment, and as a carrier for insecticides. For some uses, by-product gypsum requires purification before use as a substitute for the natural material. The Federal Government is trying out a new paving material composed largely of gypsum and lesser amounts of trash and garbage (Oil, Paint, and Drug Reporter, 1971).

MARKET POTENTIAL

The annual value of all gypsum products sold in the United States has exceeded $400,000,000 for the past several years, according to U. S. Bureau of Mines statistics (1968, 1969). If by-product gypsum is to obtain a share of this market, it must use its natural advantages of low cost and "place value" (i.e., nearness of a deposit to its point of use). The latter is of great importance in Illinois, which has no workable deposits of natural gypsum (Appleyard, 1970, p. 1, fig. 1).

CONCLUSIONS

Large quantities of waste gypsum accumulating at various sites in Illinois are now being considered as secondary mineral sources. The potential uses of by-product gypsum suggested above, its low cost, and the lower transportation costs involved in its use in Illinois may stimulate interest in its economic potential.

The quality of by-product gypsum, how it differs from chemically pure gypsum, and how it will behave as a substitute should be considered for each particular use.
REFERENCES


Chemical Week, 1971, New acid route gets the test: Chem. Week, v. 109, no. 12, p. 67.


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