ILLINOIS STATE GEOLOGICAL SURVEY

John C. Frye, Chief

ILLINOIS MINERALS NOTE 50

BY-PRODUCT GYPSUM IN ILLINOIS — A NEW RESOURCE?

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

URBANA, ILLINOIS 61801

MARCH 1973

BY-PRODUCT GYPSUM IN ILLINOIS— A NEW RESOURCE?

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

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 $CaSO_4 \cdot 2H_2O$, 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 ($CaSC_4 \cdot \frac{1}{2}H_2O$). 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.

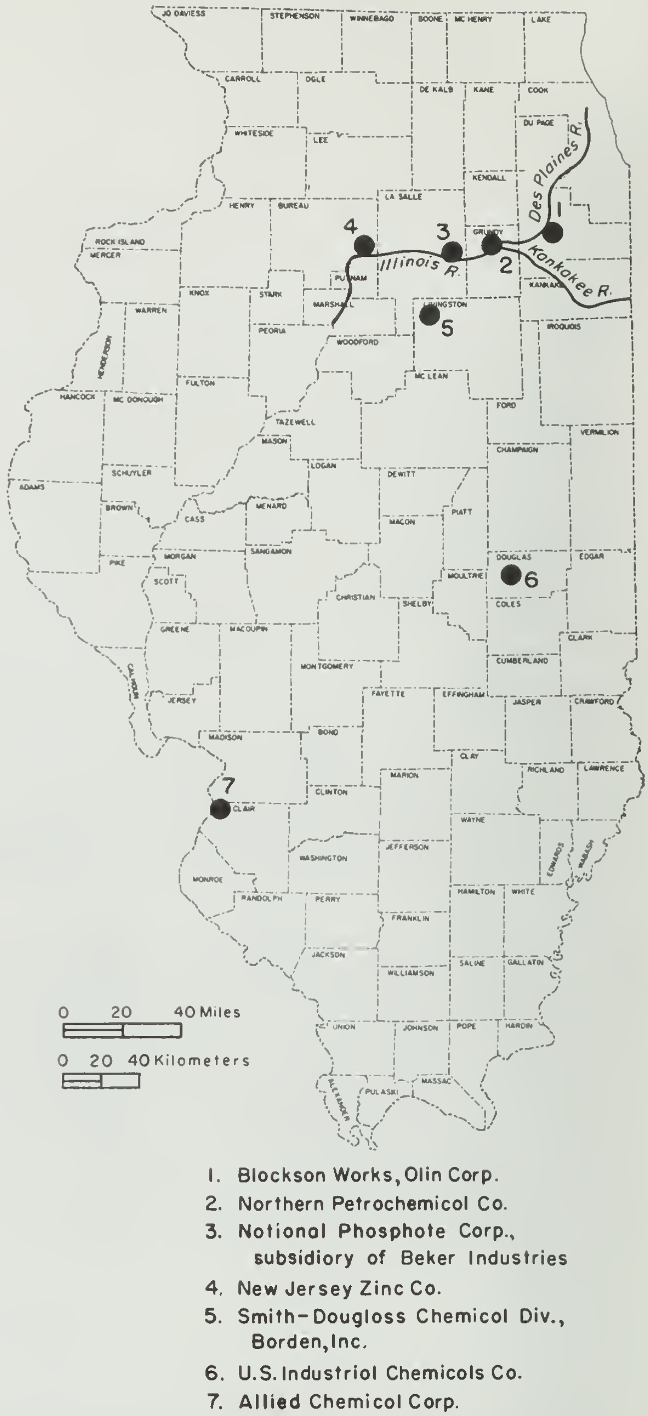


Fig. 1 - Locations of the seven major Illinois deposits of by-product gypsum. At the time of sampling, Hooker Chemical Division, Occidental Chemical Company, owned the deposit at location 3. On January 1, 1973, the National Phosphate Corporation took over the operation.

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 $Ca_{10}(PO_4)_6F_2$, 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_3O_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 ($CaSO_4 \cdot nH_2O$), approximating that of mineral gypsum, is stockpiled 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

TABLE 1—SPECIFIC LOCATIONS AND ESTIMATED TONNAGES OF BY-PRODUCT GYPSUM DEPOSITS IN ILLINOIS

Site no.	Company name	Millions of tons (est.)	County	Mailing address	Location Sec.	Location T.	Location R.	Fig. no.
1	Blockson Works, Olin Corp	> 5	Will	P.O. Box 130, Joliet, IL 60434	31	35N	10E	2A
2	Northern Petrochemical Co. (Norchem)	> 1	Grundy	P.O. Box 459, Morris, IL 60450	28	33N	8E	2B
3	National Phosphate Co., Beker Industries	> 1	La Salle	P.O. Box 88, Marseilles,IL 61341	20-21	33N	5E	2C
4	New Jersey Zinc Co.	1	Bureau	Depue, IL 61322	25-26	16N	10E	2D
5	Smith-Douglass Chemical Div., Borden, Inc.	1	Livingston	P.O. Box D, Streator, IL 61364	7	30N	4E	2E
6	U.S. Industrial Chemicals Co. (U.S.I.)	> 1.5	Douglas	P.O. Box 218, Tuscola, IL 61953	30-31	16N	8E	2F
7	Allied Chemical Corp. (Allied)	> 1	St. Clair	East St. Louis, IL 62207	3	2N	9W	2G

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 lathanum (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.

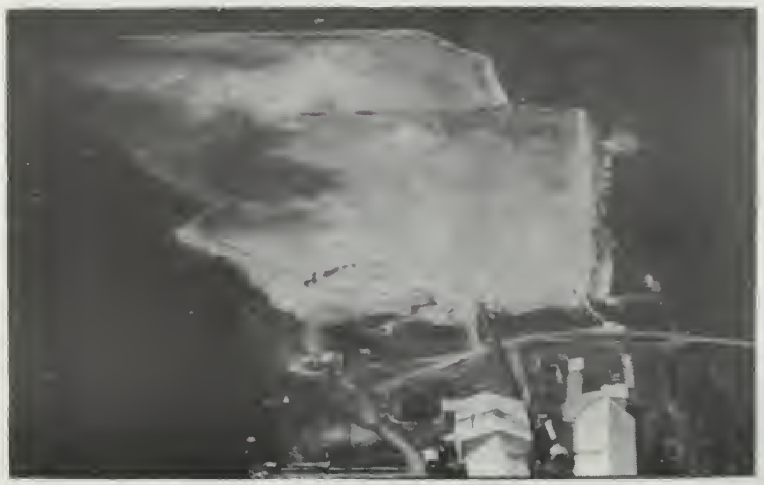
In general, the waste gypsums are composed of subspherical, radially overgrown aggregates with some varieties of either cruciform or single euhedral (rhombic) crystals (table 3). The National Phosphate sample (fig. 3C) contains more single rhombs than the others. The New Jersey Zinc sample (fig. 3D) 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.

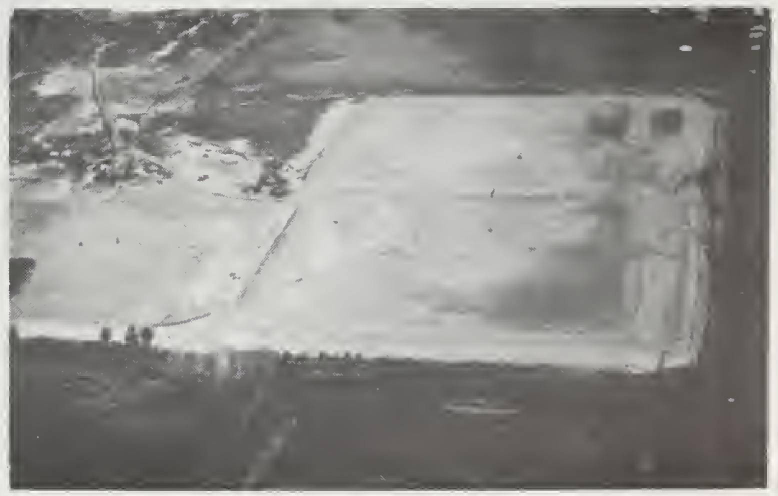
Fig. 2 - Aerial views (A through G) of by-product gypsum storage.

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

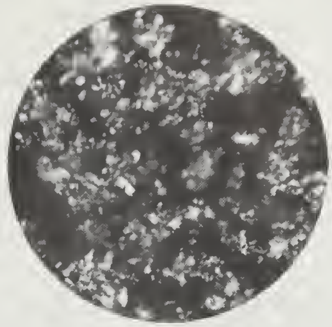
G. ALLIED CHEMICAL CORPORATION pond near East St. Louis. Currently in use.

TABLE 2—CHEMICAL ANALYSES OF BY-PRODUCT GYPSUM AND WALLBOARD

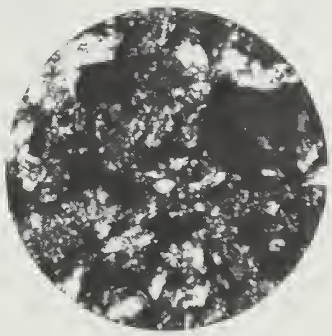
Site no., company, and sample location	Major elements (%)						Loss on ignition (%)	Minor or trace elements (%)						
	CaO	SO_3	P_2O_5	F	SiO_2	Fe_2O_3		Mn	Pb	Cu	Ti	La	U	MgO
1. Blockson														
Old pond - center	37.23	33.84	0.99	0.98	0.72	0.26	13.34	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.07
Old pond - berm	36.59	26.51	0.91	0.85	0.16	0.29	15.32	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.02
New pond - center	37.44	30.25	1.03	1.06	0.11	0.34	12.69	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.00
New pond - berm	37.91	31.23	0.72	1.57	0.44	0.34	10.93	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.11
2. Norchem (inoperative)														
Pond - center	34.55	36.11	0.67	0.72	5.77	0.32	11.09	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.24
Pond - berm	34.73	43.92	0.70	0.73	5.99	0.35	9.72	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.00
3. National Phosphate Corp.														
Inner pit	32.50	42.37	0.96	0.76	5.85	0.07	17.28	<0.05	<0.002	<0.001	<0.01	0.0057	<0.0009	—
Outer berm	34.60	46.80	1.20	0.79	2.19	0.03	14.58	<0.02	<0.001	<0.001	<0.01	0.0194	<0.0008	—
4. New Jersey Zinc														
Inner pit	31.50	39.47	1.35	1.21	15.13	0.14	10.94	<0.05	<0.005	<0.001	<0.01	0.0060	<0.0005	—
Outer berm	35.60	46.53	1.35	0.42	6.13	0.07	10.00	<0.05	<0.002	<0.001	<0.01	0.0054	<0.0005	—
5. Smith-Douglass														
Composite sample	38.60	51.19	1.13	0.81	1.34	0.03	6.90	<0.02	<0.001	<0.001	<0.01	0.006	<0.0019	—
6. U.S.I. (inoperative)														
Composite sample	33.20	42.88	1.01	0.79	5.06	0.03	16.47	<0.01	<0.001	<0.001	<0.01	0.0053	<0.0007	—
7. Allied														
Composite sample*	40.41	54.29	0.51	1.77	0.28	0.12	<5.95	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	—
8. Commercial wallboard														
Composite sample	32.50	38.43	0.10	0.00	0.43	0.00	23.10	<0.01	n.d.	<0.001	n.d.	0.0003	<0.0004	—

* Al_2O_3 = 0.57   n.a. = no analysis   n.d. = not detected

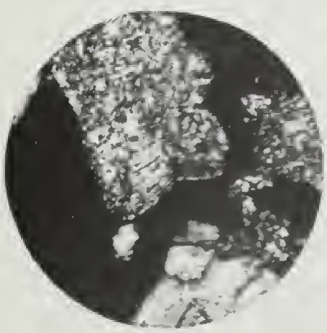
A. Rock gypsum from Shoals, Ind.



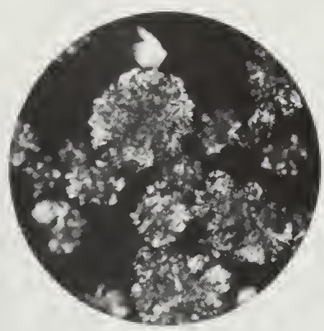
B. Commercial wallboard



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 3—WASTE GYPSUM: SOLUTION ANALYSES AND DESCRIPTION OF CRYSTAL STRUCTURE

Site no, company, and sample location	CaO (%)	SO_4 (%)	P_2O_5 (%)	F (ppm)	pH	Fig. no.	Description
1. Blockson							
Old pond - center	0.28	0.45	0.01	18	5.2		"Ghost" aggregates—indicative of leaching by meteoric (rain) water.
Old pond - berm	0.28	0.48	0.02	13	5.0		
New pond - center	0.24	0.41	0.02	18	4.9		Radially overgrown aggregates and individual smaller crystals of anhedral shape.
New pond - berm	0.26	0.45	0.03	26	4.6		
2. Norchem (inoperative)							
Pond - center	0.28	0.48	0.02	27	4.8	3E	Large, spherical, radially overgrown aggregates (correlate with granular, free-flowing, bulk characteristics).
Pond - berm	0.24	0.41	0.02	25	4.7	3E	
3. National Phosphate Corp.							
Inner pit	0.28	0.49	0.02	18	4.8	3C	Small rhombic crystals and irregular aggregates.
Outer berm	0.29	0.49	0.02	26	4.9	3C	
4. New Jersey Zinc							
Inner pit	0.29	0.48	0.10	17	4.5	3D	Large, radially overgrown aggregate crystals and large, foliate, zoned or layered crystals.
Outer berm	0.28	0.45	0.16	19	3.3	3D	
5. Smith-Douglass							
Filter cake sample	0.30	0.44	0.07	29	3.6		Spherical, radially overgrown aggregate crystals; cruciform crystals; single euhedral crystals.
6. U.S.I. (inoperative)							
Composite plant sample	0.28	0.49	0.04	19	4.6		Spherical aggregates with crystal dust.
7. Allied							
Composite plant sample	n.a.	n.a.	n.a.	n.a.	n.a.		Spherical, radially overgrown aggregates; dust; cruciform crystals; rare single euhedral crystals.
8. Natural rock gypsum							
Shoals, Ind.	0.23	0.50	<0.01	0.42	6.1	3A	Large, rhombic, single crystals; smaller crystal fragments; dust.
9. Commercial wallboard	0.23	0.40	<0.01	1.2	6.2	3B	Mostly spherical aggregates with some dust.

n.a. = no analysis.

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 (SO_4), phosphorus (P_2O_5), 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 SO_4, 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 P_2O_5) 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 AlF_5^{-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 (Al_2O_3) 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 (SO_2) 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

Aldrich, D. G., and W. R. Schoonover, 1951, Gypsum and other sulfur materials for soil conditioning: Univ. California Agr. Exp. Sta. Circ. 403, 12 p., Berkeley, California.

Appleyard, F. C., 1970, Evaluation of a gypsum deposit: Am. Inst. Mining Metall. Engrs., Soc. Mining Engrs., preprint 70-5-53, New York, 13 p.

Bradbury, J. C., G. C. Finger, and R. L. Major, 1968, Fluorspar in Illinois: Illinois Geol. Survey Circ. 420, p. 35-37.

Budnikov, P. P., R. D. Azelitskaya, and A. A. Lokot, 1968, Influence of added gypsum on mineral formation in alkali-containing cement clinker: Jour. Applied Chemistry, USSR (English transl.), v. 41, no. 105, p. 906-909.

Champaign-Urbana News-Gazette, 1971, Dead leaves for project: Associated Press release, Champaign-Urbana News-Gazette, Champaign, Illinois, Nov. 3, p. 9.

Chemical Engineering News, 1968, Scramble is on for processes that get sulfur from gypsum: Chem. Eng. News, v. 46, no. 9, p. 11-12.

Chemical Week, 1968, They're moving gypsum mountains: Chem. Week, v. 103, no. 5, p. 37-38.

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

Eipeltauer, Edward, 1958, Fields of application of gypsum products: Berg- u. hüttenmänn. Monatsh. Montan. Hochschule Leoben, v. 103, p. 65-71, 85-93; Chem. Abstr., v. 52, p. 15018.

Ellwood, Peter, 1969, Turning by-product gypsum into a valuable asset: Chem. Eng., v. 76, Mar. 24, p. 106-108.

Fehrenbacher, J. B., T. D. Hinesly, P. E. Johnson, and B. A. Jones, Jr., 1967, Corn yields on natric soils after varying applications of gypsum: Univ. Illinois Agr. Exp. Sta., Illinois Research, summer issue, p. 14-15.

Fehrenbacher, J. B., R. T. Odell, P. E. Johnson, and B. A. Jones, Jr., 1966, Natric soils in Illinois: Univ. Illinois Agr. Exp. Sta., Illinois Research, winter issue, p. 5-7.

Fisons Fertilizers, Ltd., 1970, Calcium sulfate hemihydrate, suitable for use in plasters (Brit. pat. 1,202,893, R. F. Hall, 8/19/70): Chem. Abstr., v. 73, p. 89662v.

Harre, E. A., 1969, Fertilizer trends—1969: Natl. Fertilizer Devel. Center, Tenn. Valley Authority, Muscle Shoals, Alabama (F70ACD1), 103 p.

Industrial Minerals, 1970, Gypsum sulfur values: Ind. Minerals, no. 37, p. 22-25.

Kim, Jin Won, and S. W. Lee, 1968, Use of by-product phosphogypsum for portland cement retarder: Bull. Korean Ceram. Soc., v. 5, no. 2, p. 91-97; Ceram. Abstr., v. 53, no. 8, #188d (1970).

Kitchen, D., and W. J. Skinner, 1971, Chemistry of by-product gypsum and plaster, I. Identity of an important solid solution impurity: Jour. Applied Chem. Biotechnol., v. 21, no. 2, p. 53-55; II. Chemistry of cocrystalline AlF_5^{-2} during gypsum calcination and subsequent mixing of the hemihydrate with water: ibid., p. 56-60; III. Retarder insensitivity in hydrating calcium sulphate hemihydrate: ibid., no. 3, p. 65-67.

Oil, Paint and Drug Reporter, 1971, Chemical waste, garbage being used in pavement: Oil, Paint & Drug Reporter, v. 200, no. 26, p. 4.

Oil, Paint and Drug Reporter, 1973, Sulfuric acid plant running on by-product gypsum: v. 203, no. 6, p. 17.

Padhi, U. C., R. T. Odell, J. B. Fehrenbacher, and R. D. Seif, 1965, Effect of gypsum and starch on water movement and sodium removal from solonetzic soils in Illinois: Soil Sci. Soc. Am. Proc., v. 29, no. 2, p. 227-229.

Remirez, Raul, 1968, Gypsum finds new role in easing sulfur shortage: Chem. Eng., v. 75, no. 23, p. 112-114.

U. S. Bureau of Mines, 1968, Gypsum, in Minerals yearbook—1968: U. S. Bur. Mines, Dept. Interior, Washington, D.C., v. 1-2, p. 559-566.

U. S. Bureau of Mines, 1969, Gypsum, in Minerals yearbook—1969: U. S. Bur. Mines, Dept. Interior, Washington, D.C., v. 1-2, p. 547-554.

SELECTED LIST OF SURVEY PUBLICATIONS

MINERAL ECONOMICS BRIEFS SERIES

5. Summary of Illinois Mineral Production in 1961. 1962.
11. Shipments of Illinois Crushed Stone, 1954-1964. 1966.
12. Mineral Resources and Mineral Industries of the East St. Louis Region, Illinois. 1966.
13. Mineral Resources and Mineral Industries of the Extreme Southern Illinois Region. 1966.
17. Mineral Resources and Mineral Industries of the Springfield Region, Illinois. 1967.
19. Mineral Resources and Mineral Industries of the Western Illinois Region. 1967.
20. Mineral Resources and Mineral Industries of the Northwestern Illinois Region. 1967.
21. Illinois Mineral Production by Counties, 1966. 1968.
22. Mineral Resources and Mineral Industries of the Northeastern Illinois Region. 1968.
26. Evaluation of Fuels—Long-Term Factors and Considerations. 1969.
27. Illinois Mineral Production by Counties, 1968. 1970.
29. Directory of Illinois Mineral Producers. 1971.

INDUSTRIAL MINERALS NOTES SERIES

13. Summary of Illinois Mineral Industry, 1951-1959. 1961.
17. Pelletizing Illinois Fluorspar. 1963.
19. Binding Materials Used in Making Pellets and Briquets. 1964.
20. Chemical Composition of Some Deep Limestones and Dolomites in Livingston County, Illinois. 1964.
21. Illinois Natural Resources—An Industrial Development Asset. 1964.
23. Limestone Resources of Jefferson and Marion Counties, Illinois. 1965.
24. Thermal Expansion of Certain Illinois Limestones. 1966.
26. Binders for Fluorspar Pellets. 1966.
27. High-Purity Limestones in Illinois. 1966.
29. Clay and Shale Resources of Clark, Crawford, Cumberland, Edgar, Effingham, Jasper, and Vermilion Counties. 1967.
30. Lightweight Bricks Made with Clay and Expanded Plastic. 1967.
31. Clays as Binding Materials. 1967.
32. Silica Sand Briquets and Pellets as a Replacement for Quartzite. 1968.
33. A New Use for Illinois Clay Materials in Pesticide Formulations. 1968.
34. Neutron Activation Analysis at the Illinois State Geological Survey. 1968.
35. Computer-Calculated Lambert Conformal Conic Projection Tables for Illinois (7.5-Minute Intersections). 1968.
36. Beneficiation of Kaolinite Clay from Silica Sand Washings. 1968.
37. Peat and Humus in Illinois. 1969.
38. Kankakee Dune Sands as a Commercial Source of Feldspar. 1969.
39. Alumina Content of Carbonate Rocks as an Index to Sodium Sulfate Soundness. 1969.
40. Colloidal-Size Silica Produced from Southern Illinois Tripoli. 1970.
41. Two-Dimensional Shape of Sand Made by Crushing Illinois Limestones of Different Textures. 1970.
42. An Investigation of Sands on the Uplands Adjacent to the Sangamon River Floodplain: Possibilities as a "Blend Sand" Resource. 1970.
43. Lower Mississippi River Terrace Sands as a Commercial Source of Feldspar. 1970.
44. Analyses of Some Illinois Rocks for Gold. 1970.
45. Clay and Shale Resources of Madison, Monroe, and St. Clair Counties, Illinois. 1971.
46. Sideritic Concretions in Illinois Shale, Gravel, and Till. 1972.
47. Selected and Annotated List of Industrial Minerals Publications of the Illinois State Geological Survey. 1972.

ILLINOIS MINERALS NOTES SERIES

(The Illinois Minerals Notes Series continues the Industrial Minerals Notes Series and incorporates the Mineral Economics Briefs Series)

48. Illinois Mineral Production by Counties, 1970. 1972.
49. Clay and Shale Resources of Peoria and Tazewell Counties, Illinois. 1973.