Use of By-Product Phosphogypsum in Road Construction

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Phosphogypsum is a solid by-product material resulting from the production of phosphoric acid, a major constituent of many fertilizers. It has been estimated that more than 800 million tons of phosphogypsum are stockpiled in the U.S. The current production rate exceeds 60 million tons per year, with less than 2 percent being recycled at the present time. The results of the laboratory phase of a research program to develop phosphogypsum as a road base material are presented. The research program included physical and chemical characterization of the phosphogypsum, mineralogical analysis, moisture-density relations, unconfined compressive strength testing, freeze-thaw and wet-dry durability tests, and expansion testing. A comparison is made between the engineering properties of phosphogypsum and the Louisiana Department of Transportation and Development requirements for road base materials.

Phosphogypsum is a solid by-product of phosphoric acid production. Phosphoric acid is a major constituent of many fertilizers. Of the several different phosphoric acid production processes, the wet process is the most frequently used (1). In the wet process, finely ground phosphate rock, $\text{Ca}_3\text{F}_2\text{(PO}_4\text{)}_2$, is dissolved in phosphoric acid to form a monocalcium phosphate solution. Sulfuric acid, which is added to the slurry, reacts with the monocalcium phosphate to produce a hydrated calcium sulfate, which can then be separated from the phosphoric acid by filtration.

The resulting filter cake containing the hydrated calcium sulfate is called phosphogypsum. Typically, the filter cake slurry and wash solution are piped to large stockpiles where the phosphogypsum is allowed to settle.

The crystals of calcium sulfate can exist in at least three forms: anhydrite, hemihydrate, and dihydrate. The anhydrous crystal, commonly called calcium sulfate (CaSO₄), has no chemically combined water (water of hydration). The hemihydrate molecule contains one-half molecule of chemically combined water and is denoted by $\text{CaSO}_4\cdot\frac{1}{2}\text{H}_2\text{O}$. The dihydrate molecule contains two molecules of chemically combined water and is denoted by $\text{CaSO}_4\cdot2\text{H}_2\text{O}$. In this form, the mineral is commonly referred to as gypsum. Several modifications of the wet process exist, which are distinguished by the predominant type of calcium sulfate crystal that is produced. The percentages of each crystal type in a given sample influence, both directly and indirectly, the properties of the phosphogypsum. Goers (2) stated that crystal type and size affect the amount of phosphoric acid remaining in the filter cake after filtration, which, in turn, may affect the engineering properties of the phosphogypsum (3). Leggo and Myrick (4) noted that the temperature of the reaction mass and the phosphoric acid concentrations are the controlling factors governing the degree of hydration of the calcium sulfate. Most of the wet-process phosphoric acid produced in the world is made by the dihydrate process or some modification of the process.

As a general rule, 4.5 to 5.5 tons of phosphogypsum are generated for every ton of phosphoric acid produced (5). The demand for phosphoric acid further magnifies the problem of efficiently and economically dealing with growing phosphogypsum stockpiles. In 1980, phosphogypsum was generated at an annual rate of 840,000 tons in Australia alone (6). In 1979, Japan was producing phosphogypsum at a rate of 2,748,000 metric tons per year (7). In the United States, phosphogypsum is currently being produced at a rate of 40 million tons per year. In Florida, more than 334 million tons of phosphogypsum had been stockpiled by 1980. At that time, phosphogypsum production in Florida was 33 million tons per year. Therefore, as of 1990, there are approximately 650 million tons of phosphogypsum in Florida alone. Long-term projections indicate that more than 1 billion tons will be stockpiled in Florida by the year 2000 (8). In Louisiana, more than 95 million tons of phosphogypsum have been stockpiled as of 1989 (9). Another 25 million tons of phosphogypsum also exist in the Houston area (10). Obviously, these large quantities of material must be dealt with before they become unmanageable. Similar problems with use and disposal of this material also exist in Europe and Canada (11).

Other by-product gypsiums (BPG) that are available in large quantities in the United States include fluorogypsum, flue gas desulfurization (FGD) gypsum, and titanogypsum. These BPG designations are based on the specific chemical process from which the material is produced. According to the Electric Power Research Institute, 20 million tons of FGD gypsum are generated annually in the United States (D. Golden, personal communication, 1991). With the enactment of the recent Clear Air Act legislation, the current plants will probably add another 20 million tons per year of FGD gypsum. The total current inventory of the material is approximately 150 million tons. In 40 years, it is estimated that the amount of FGD gypsum will quadruple.

The amount of phosphogypsum that has been disposed of to date plus the current rate of production indicate the seriousness of the problem. The disposal of such material...
must address several factors to develop a cost-effective and environmentally sound practice. Such factors include the following:

1. Runoff from stockpiles may be acidic and a potential threat to surface and groundwater resources.
2. The long-term effects of low-level radioactive emissions from stockpiled phosphogypsum are presently unknown.
3. The availability and high cost of land for disposing of the material are becoming major concerns [stockpiles of phosphogypsum covered more than 1,773 acres of Florida land in 1972 (12)].

As stockpiles continue to grow and environmental constraints become more stringent, widespread uses of phosphogypsum must be developed. Ideally, such uses would involve large tonnages of phosphogypsum preferably in its natural or as-produced state. One such possible use could be as a base material in highway construction. To enhance the engineering properties of most phosphogypsum, some cementitious or pozzolanic binder must be added to the system.

OBJECTIVE

The main objective of this paper is to summarize the pertinent results obtained from the laboratory testing program to evaluate the properties and behavior of cement-stabilized phosphogypsum when used as a base material. Recommendations for additional studies are also presented.

MATERIALS

Phosphogypsum

In Louisiana, Freeport-McMoran, Inc. (FMI) uses the dihydrate modification of the wet process to produce phosphate fertilizers. Therefore, the phosphogypsum used in this study is in the dihydrate form, that is, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

An isolated mesa was formed on the disposal pile at the Uncle Sam plant in July 1985. This mesa, measuring approximately 500 by 600 ft, had an elevation of about +6 to +10 ft above the top of the active stack area. All phosphogypsum used in the FMI study was collected from the top few inches of the stack and from selected locations in the stockpiles. Characterization of the phosphogypsum will be discussed in later sections of the paper.

Portland Cement

Different types of portland cement were used in the research program. They are as follows:

- Type I Citadel Demopolis cement (11 percent $\text{C}_3\text{A}$),
- Type II Ideal fine grind cement (7 percent $\text{C}_3\text{A}$),
- Type II Dundee cement (5.6 percent $\text{C}_3\text{A}$),
- Type II Gifford-Hill cement (5 percent $\text{C}_3\text{A}$),
- Type V Gifford-Hill cement (5 percent $\text{C}_3\text{A}$),
- Type V Citadel Leharve cement (5 percent $\text{C}_3\text{A}$),
- Type V United cement (3 percent $\text{C}_3\text{A}$), and
- Type II Lone Star cement (0 percent $\text{C}_3\text{A}$).

The use of various cements is necessary because of the influence of the tricalcium aluminate ($\text{C}_3\text{A}$) present in the cement on the strength development and expansive characteristics of stabilized phosphogypsum mixtures. Most of the cements are commercial cements that will meet the requirements of ASTM C150.

EXPERIMENTAL INVESTIGATION

FMI took the lead in investigating the potential use of phosphogypsum. From 1985 through 1989, they conducted a laboratory investigation of the phosphogypsum produced at their Uncle Sam and Faustina plants (13). Their research program included physical and chemical characterization, mineralogical analysis, moisture-density relations, unconfined compressive strength testing, freeze-thaw and wet-dry durability tests, water submersion tests, and expansion testing. The following sections summarize the results of these studies and include recommendations for further study.

Chemical and Physical Properties

The chemical and physical characterization of phosphogypsum was carried out as part of the research program. The chemical analysis of the material is given in Table 1. The data presented in Table 1 represent a range of values obtained on

![FIGURE 1 Particle size distribution of pump sand and phosphogypsum.](image-url)
several samples. In addition, a number of trace elements are present in phosphogypsum. Typical concentrations of these elements are given in Table 2. According to Table 2, lead concentration of fresh phosphogypsum will exceed the EPA leachate standards. However, leachate samples taken from cement or fly ash stabilized phosphogypsum mixtures will meet the EPA leachate requirements.

The physical properties of phosphogypsum, such as moisture content, specific gravity, and fineness, are presented in Table 3. A temperature of 55°C (131°F) was used to determine the free moisture in the phosphogypsum. Temperatures higher than 60°C (140°F) tend to convert the dihydrate phosphogypsum (CaSO4·2H2O) to the hemihydrate form (CaSO4·½H2O). Higher temperatures will also cause a significant amount of fracture and delamination of the phosphogypsum particles. These tests were conducted on three phosphogypsum samples dried at three temperatures (room temperature, 140°F, and 257°F).

Table 3 also indicates that more than 75 percent of the phosphogypsum particles will pass the #200 sieve.

**Morphological Analysis**

Morphology was investigated by optical and scanning electron microscopy (SEM). Particles were generally radiating agglomerates of platelets. Some of the aged or weathered materials were more rounded and denser. A few samples showed unagglomerated platelets. Figure 2 shows a typical micrograph of phosphogypsum sampled from the Uncle Sam stockpile. It shows the friable texture of the phosphogypsum.

**Mechanical Properties**

Strength development in phosphogypsum mixtures can be achieved through stabilization with either portland cement, lime, fly ash, or combinations thereof. To determine the strength development, the optimum moisture content and maximum dry density values were first established using a standard Proctor laboratory compaction test series. An optimum moisture content of 21.5 percent and a maximum dry density of 88.5pcf were determined for unstabilized phosphogypsum mixtures. Typical moisture-dry density relations for phosphogypsum mixtures stabilized with 5 percent Type II Ideal fine ground cement are shown in Figure 3. Samples were either prepared in accordance with ASTM D1557—Method A (modified Proctor) or as specified by ASTM D698 (standard Proctor). The latter method is essentially the same as the Louisiana Department of Transportation and Development (LDOTD) Test Method TR418—Method B. As can be seen in Figure 3, higher maximum dry density and lower optimum moisture values were obtained with the higher compaction energy.

The following procedure was adopted in the preparation of the cement-stabilized phosphogypsum specimens. Raw phosphogypsum was initially dried at a temperature of 131°F to a constant weight. The cement was added on a dry weight basis. The phosphogypsum and cement were dry mixed for 30 sec. Water was added as necessary to bring the mixture to the required optimum moisture (water was taken as the percentage of the total dry materials). The mixture of phosphogypsum, cement, and water was mixed for about 2.5 min to obtain a visibly homogeneous blend. The materials collected at the bottom of the mixing bowl following mechanical mixing were thoroughly mixed with the rest of the material by hand. The mixture was covered at all times with a towel during the compaction process to avoid the evaporation of water.

After completing the compaction series, duplicate specimens were prepared at optimum moisture content for strength determination using the unconfined compression test (ASTM D1633). Most molded specimens were cured in plastic bags and were subjected to a 4-hr soak in water before compression testing. The 7- and 28-day compressive strength results for cement-stabilized phosphogypsum mixtures compacted in accordance with the standard and modified Proctor methods are shown in Figures 4 and 5. Modified Proctor compaction produced higher dry densities and resulted in 7- and 28-day com-
FIGURE 2 Micrograph of phosphogypsum from the Uncle Sam stockpile.

FIGURE 3 Moisture-dry density relations of cement-stabilized phosphogypsum mixtures.

FIGURE 4 Seven-day unconfined compressive strength for Type II Ideal fine grind cement-stabilized phosphogypsum mixtures prepared under different compaction procedures.

FIGURE 5 Twenty-eight-day unconfined compressive strength for Type II Ideal fine grind cement-stabilized phosphogypsum mixtures prepared under different compaction procedures.

Pressive strengths about 130 and 90 percent higher, respectively, than obtained for specimens prepared using standard Proctor compaction.

LDOTD requires a minimum 7-day compressive strength of 250 psi for soil-cement mixtures (Test Method TR432—Method B). From Figure 4, a minimum of 8.7 percent cement will satisfy the required strength criteria if standard Proctor compaction is used. However, about 4 percent cement is needed to achieve a minimum 7-day strength of 250 psi if modified Proctor compaction is used. Therefore, the question of the
density that can be achieved in the field becomes of great significance.

Figure 6 indicates the effect of curing time and cement content on the compressive strength of cement-stabilized phosphogypsum mixtures. With an increase in cement content and curing period, there is a corresponding increase in the unconfined compressive strength.

Figure 7 shows that the use of either Type II or V cements will have little effect on the strength development in stabilized phosphogypsum mixtures. Both are sulfate-resistant cements, and similar engineering behavior (in particular, strength and sulfate attack resistance) should be expected when using both stabilizers with phosphogypsum.

Phosphogypsum samples collected at different depths within a stockpile may have different pH values. This will influence the strength of various cement-stabilized phosphogypsum mixtures. Some of the added cement will be exhausted in neutralizing the more acidic phosphogypsum. Quality control is an important issue in the use of phosphogypsum stockpiles. A study that addresses the influence of pH on the strength of cement-stabilized phosphogypsum mixtures is currently under way at the Institute for Recyclable Materials.

Water Submersion Testing

The effects of long-term water submersion on the strength of specimens of stabilized phosphogypsum were investigated. Initially, the specimens were cured for either 1 or 4 weeks in double-sealed plastic bags. The test conditions then called for submersion of specimens in a water bath with the water flowing at a rate of 600 mL/min (equivalent to a replacement volume of the water in the bath every 2 hr). The specimens were dried with a towel and immediately tested in unconfined compression. This test was developed to simulate the worst possible case of complete saturation of the base material during a rainy season. Figure 8 shows that all of the specimens prepared using the Type II Lone Star cement showed a decrease in unconfined compressive strength after water submersion for as little as 1 week. Phosphogypsum stabilized with 8 percent Type II Lone Star cement showed an unconfined compressive strength of 311 psi after 1 week bag cured. However, the strength decreased to 235 psi for similar stabilized phosphogypsum mixtures submerged under water for 23 weeks. On the other hand, the specimens prepared with Type II Dundee cement and Type II Ideal fine grind cement along with the additive microsilica showed an increase in strength after submersion. Phosphogypsum stabilized with 8 percent Type II Dundee cement showed an unconfined compressive strength of 269 psi after 1 week bag cured. When similar
stabilized phosphogypsum mixtures were submerged under water for 60 weeks, the strength increased to 350 psi.

Expansion Testing

In an effort to determine the suitability of a given Portland cement for use in stabilizing phosphogypsum, a long-term reactivity test was used. The test was conducted using equipment specified by ASTM Test Methods C511 and C490. Stabilized phosphogypsum and pump sand specimens were prepared using 4-in.-diameter by 11.25-in.-high molds, and the length change of test specimens was measured along the longitudinal axis using a comparator. The specimens were cured for approximately 3 years in humidity bath cabinets at 100°F and 100 percent relative humidity. Figure 9 shows the expansion results of phosphogypsum and pump sand specimens stabilized with different types of cement. The most expansion was observed in the phosphogypsum specimens prepared using Type I Citadel Demopolis cement with 11 percent C₃A content. On the basis of these results, it is noted that there is an increase in the expansion of stabilized mixtures of phosphogypsum and cement as the C₃A content in the cement increases. Also, the expansion continues but at a decreasing rate as the curing period increases. The least expansion was observed in the pump sand specimens prepared using Type I Citadel Demopolis cement.

Scanning electron microscopy tests conducted on phosphogypsum mixtures stabilized with 10 percent Type I Citadel Demopolis cement indicated the formation of ettringite crystals. Long slender prismatic needles that characterize ettringite crystals were observed. This formation may well be related to the phenomenon of sulfate attack expansion in high sulfate mixtures prepared using cement or lime as stabilizers.

Freeze-Thaw Test Results

Porous materials containing moisture are susceptible to damage under repeated cycles of freezing and thawing (frost attack).

Stabilized phosphogypsum specimens were compacted at optimum moisture content using ASTM Procedure D698 (standard Proctor compaction) and were subjected to freeze-thaw cycles using modifications of AASHTO Procedure T-136. The freeze-thaw test involved subjecting the test specimens to 12 cycles of freezing and thawing followed by measurements of weight losses and volume changes. One freeze-thaw cycle was accomplished by placing the specimens at −10°F for 24 hr and then for another 24 hr at 70°F. After each cycle, some specimens were brushed and then weighed to determine weight loss. Other specimens remained unbrushed for control measurements. Final dry weights of the molded specimens were determined after placing them in an oven at 131°F. Table 4 presents the results of the freeze-thaw durability tests. The

<table>
<thead>
<tr>
<th>TABLE 4</th>
<th>FREEZE-THAW DURABILITY TEST RESULTS FOR CEMENT-PUMP SAND-PHOSPHOGYPSUM MIXTURES</th>
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<tbody>
<tr>
<td>Method</td>
<td>Mix Design</td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
</tr>
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<td>100</td>
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</table>

Notes: 1. All tests used Type II Dundee cement with exception noted.
2. *Type II Lone Star cement.
3. Cure time for all tests using Type II Dundee cement was 651 days.
4. Cure time for the test using Type II Lone Star cement was 202 days.
5. N/A: not available.
data indicate that a maximum volume loss of 5.8 percent is produced for phosphogypsum mixtures stabilized with 8 percent Type II Dundee cement. An increase in cement content will decrease the volume change and weight loss in a freeze-thaw test. The use of 8 percent Type II Lone Star cement with phosphogypsum produced a volume loss of 5.0 percent after the completion of the freeze-thaw test. The weight loss behavior exhibited by the specimens in this test series will meet the recommended Portland Cement Association (PCA) maximum weight loss of 10 percent for siltlike materials (phosphogypsum falls under this category). Thus, these results generally indicate that stabilized phosphogypsum mixtures should perform satisfactorily as base materials subject to frost action.

**Wet-Dry Test Results**

Cement-stabilized systems may be subjected to swelling and shrinkage produced by repeated wetting and drying of the hardened system. In a state such as Louisiana, where rainfall exceeds the amount of evaporation and rainfall, humidity, and temperature are high during the summer, the wet-dry durability test is of special significance.

Stabilized phosphogypsum specimens were prepared using standard Proctor compaction and were subjected to wet-dry cycles using modifications of AASHTO Procedure T-135. The wet-dry test involves subjecting the test specimens to 12 cycles of wetting and drying followed by measurements of weight loss and volume change. One wet-dry cycle was accomplished by submerging the specimens in water at room temperature for 5 hr and then for another 42 hr in an oven at 131°F. After each cycle, some specimens were brushed to determine weight loss. Other specimens remained unbrushed for control measurements. Final dry weights of the molded specimens were determined by placing them in an oven at 131°F. Table 5 presents the results of the wet-dry durability tests. The data indicate that, with an increase in cement content, there is a decrease in the volume change and weight loss in a wet-dry test. All weight loss data will meet the recommended PCA-specified maximum weight loss of 10 percent. No brushed weight loss data are available for the phosphogypsum mixture stabilized with 8 percent Type II Lone Star cement. However, the volume loss observed for the phosphogypsum mixture stabilized with 8 percent Type II Lone Star cement was 10.2 percent, which may be significant under repeated wet-dry cycles. This cement had a lower C₃A content than the Type II Dundee cement. Thus, the amount of C₃A present in the cement may influence the results of the wet-dry test.

**CONCLUSIONS**

The laboratory studies completed to date warrant the following conclusions:

1. The laboratory results indicate that portland cement-stabilized phosphogypsum mixtures can be successfully used as road base and subbase materials.
2. The type and amount of Portland cement will significantly influence the performance of stabilized phosphogypsum mixtures.
3. Moisture content and compactive effort have a significant influence on the dry density and compressive strength of stabilized phosphogypsum mixtures.
4. Durability tests indicate satisfactory performance of selected stabilized phosphogypsum mixtures.
5. Selection of portland cement type in stabilizing phosphogypsum systems should be approached cautiously. The reaction between the tricalcium aluminate present in the cement and the sulfates in the phosphogypsum can lead to the formation of ettringite and thaumasite crystals. Eventually, cracking of the pavement may occur.

**TABLE 5 WET-DRY DURABILITY TEST RESULTS FOR CEMENT-PUMP SAND-PHOSPHOGYPSUM MIXTURES**

<table>
<thead>
<tr>
<th>Method</th>
<th>Mix Design</th>
<th>Volume Change (%)</th>
<th>Uncorrected Brushed Weight Loss (%)</th>
<th>7-Day Strength Bag Cure (psi)</th>
<th>After Test Brushed Strength (psi)</th>
<th>Unbrushed Strength (psi)</th>
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<tr>
<td></td>
<td>Phosphogypsum (%)</td>
<td>Cement (%)</td>
<td>Sand (%)</td>
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</table>

**Notes:**
1. All tests used Type II Dundee cement with exception noted.
2. *Type II Lone Star cement.
3. Cure time for all tests using Type II Dundee cement was 651 days.
4. Cure time for the test using Type II Lone Star cement was 202 days.
5. N/A: not available.
RECOMMENDATIONS

Additional laboratory studies are needed to investigate the underlying phenomenon for the expansion that was observed in the cement-stabilized phosphogypsum specimens. A study of this kind will be initiated soon at the Institute for Recyclable Materials, College of Engineering, Louisiana State University to enhance our knowledge of the fundamental chemical and physical mechanisms contributing to the stability and strength of cement-stabilized phosphogypsum mixtures. Furthermore, flexural fatigue and dynamic modulus testing will be included in the follow-up testing program.

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REFERENCES


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