Environmental and Engineering Properties of Flue Gas Desulfurization Gypsum

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As a result of sulfur oxides (SOx) emissions control for power plants burning lignite or sulfur coals, 18,000,000 Mg (20 million tons) of flue gas desulfurization (FGD) gypsum are generated annually in the United States. One application under which the material is being considered for use is in road base-subbase construction. Presented in this paper is a summary of the physical and chemical characterization, the radiological and leachate analysis, and the mechanical properties of FGD gypsum. Preliminary laboratory data indicate that cement stabilized FGD gypsum mixtures should perform satisfactorily in road base-subbase construction. However, further laboratory and field data are needed to fully understand and evaluate the properties of these materials.

Ever-increasing highway construction costs coupled with a geographic shortage of good-quality materials continually spur interest in the search for alternate construction methods and materials. In many locations, such as in the Gulf Coast area, aggregates must be hauled several hundred miles, thereby adding significant transportation charges to the cost of the construction. One material currently existing in large quantities in Florida, Louisiana, and Texas that could help relieve this problem is by-product gypsum. By-product gypsiums are usually given designations to reflect the specific chemical process that produced them (e.g., phosphogypsum, fluorogypsum, FGD gypsum, and so on).

FGD gypsum, a by-product of sulfur oxides recovery operations at power plants burning coals, is one such system. Sulfur, a natural contaminant of coal, is almost completely converted to sulfur oxide when coal is burned. FGD processes result in SOx removal by inducing exhaust gases to react with a chemical absorbent as they move through a scrubber (J). The absorbent (limestone, calcium hydroxide, or calcium oxide) is dissolved or suspended in water forming a solution or slurry that can be sprayed or otherwise forced into contact with the escaping gases.

Pumped in a slurry form to stockpiles, this material consists predominantly of either calcium sulfate (CaSO4) or calcium sulfate (CaSO3) crystals. The crystals can further exist in at least three forms: anhydrite, hemihydrate, or dihydrate. This material has a grain size distribution similar to silt and is very friable in nature.

According to Dean Golden (unpublished data), 18,000,000 Mg (20 million tons) of FGD gypsum are generated annually in the United States. With the enactment of the recent Clean Air Act legislation, the current plants will probably add another 18,000,000 Mg (20 million tons)/year of FGD gypsum. The total current inventory of the material is approximately 136,000,000 Mg (150 million tons). In 40 years, it is estimated that the amount of FGD gypsum will quadruple.

During the past 7 years, Texas A&M University has been involved in an ongoing research effort involving the development of cost-effective use of FGD gypsum with the objective of evaluating its potential for use in road bases and subbases (2–4).

Two experimental roads were completed in 1988 and 1989 (2,3). Cement and cement-fly ash stabilized FGD gypsum test sections were used as base materials. However, some road sections did not perform satisfactorily and had to be replaced. Contributing factors for this poor performance of the material include stabilizers selection, construction practices, and subgrade conditions.

OBJECTIVE

The main objective of this paper is to summarize the results of physical, chemical, radiological, leachate, and mechanical tests performed on FGD gypsum. Particular attention is given to the use of FGD gypsum as a subbase-base material in road construction.

MATERIALS

FGD Gypsum

The FGD gypsum used in the research study is produced by the Texas Utilities Generating Company (TUGCO) at their Martin Lake Power Plant in Tatum, Texas. The material consists mainly of calcium sulfate crystals and is currently being produced at 18 other plants in Texas at a total rate of 900,000 Mg (1 million tons)/year. FGD gypsum was collected in 45, 18.9-L (5-gall) capacity buckets over a period of 90 days for the characterization studies.

Portland Cement

The portland cement used in the research program was a commercial Type II cement meeting the requirements of ASTM
C150. The cement was a sulfate-resistant cement with a tricalcium aluminate (C₃A) content of 3.06 percent. The bulk cement was purchased from Texas Industries of Midlothian, Texas.

EXPERIMENTAL RESULTS

The research program encompassed physical and chemical characterization, radiological and leachate analysis, moisture-density relations, unconfined compressive strength testing, and dynamic modulus and flexural fatigue tests. The following sections summarize the results of these studies and include recommendations for further study.

Physical Properties

The physical properties of FGD gypsum are as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Averagea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free moisture</td>
<td>14%</td>
</tr>
<tr>
<td>Structural moisture</td>
<td>26%</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.30</td>
</tr>
<tr>
<td>&lt; #325 sieve</td>
<td>53%</td>
</tr>
</tbody>
</table>

aAverage of 90 samples.

A free moisture of 14 percent was obtained by drying the material at 40°C (104°F). At temperatures above 70°C (158°F), all chemically or structurally bonded water (about 26 percent) will also be removed (5). FGD gypsum exhibits little or no plasticity. Based on the Unified Soil Classification System (USCS), the material would be classified as ML (a silt with little or no plasticity). One hundred percent of the material will pass the No. 4 sieve and more than 60 percent will pass the No. 200 sieve. The absence of plasticity in gypsum and its silt-sized grain-size distribution have been confirmed by Blight (6) and Knight et al. (7).

Chemical Properties

The chemical breakdown of FGD gypsum is as follows:

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>24</td>
</tr>
<tr>
<td>SO₄₂⁻</td>
<td>54</td>
</tr>
<tr>
<td>CO₂</td>
<td>3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.7</td>
</tr>
<tr>
<td>Inert</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The material consists mainly of calcium (Ca) and sulfate (SO₄₂⁻) crystals. The pH of FGD gypsum is approximately 6.6. Also, a number of trace elements are present in the material. Typical leachate concentrations of these elements are listed in Table 1. The concentrations of the leachable metals from fresh FGD gypsum are well below the EPA Leachate Standards. The leachate analysis on the samples was conducted in 1988 in accordance with the Extraction Procedure (EP) toxicity characteristic test. However, in March of 1990, the Environmental Protection Agency (EPA) replaced the EP toxicity test by the Toxicity Characteristic Leaching Procedure (TCLP). No TCLP test data are available on fresh or stabilized FGD gypsum.

Environmental Characterization

The environmental testing program consisted of radiological and leachate testing.

Radiological Testing

A radiological evaluation was conducted by Erdman and Vasquez (8) on 12 samples of FGD gypsum. The testing included an analysis of the existing gross beta and alpha activities as well as the Radium-226 content. The results of this analysis are given in Table 2. No significant radiological differences were found between any of the 12 samples. The Radium-226 concentrations were in the same range as literature values (0.1 to 0.3 pCi/g) for typical soils (9) and (0.3 to 5.3 pCi/g) for cement (10). Erdman and Vasquez conclude in the report (8) that "all of the FGD gypsum samples are radiologically similar and pose no greater risk than typical construction materials in use today."

Leachate Testing

The leachate analysis of the trace elements present in a mixture of FGD gypsum stabilized with 11 percent Type II portland cement was conducted using the EP Toxicity test. The results, which are listed in Table 3, indicate that the leachate quality is well within the EPA Leachate Standards. It is well
TABLE 3 Results of the Leachate Analysis of a Mixture of FGD Gypsum Stabilized with 11% Type II Portland Cement

<table>
<thead>
<tr>
<th>Element</th>
<th>EP Toxicity* (mg/L)</th>
<th>EPA Leachate Standards (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>&lt;0.01</td>
<td>10.0</td>
</tr>
<tr>
<td>Ba</td>
<td>&lt;0.50</td>
<td>100.0</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.005</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>0.19</td>
<td>5.0</td>
</tr>
<tr>
<td>Pb</td>
<td>0.17</td>
<td>5.0</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.005</td>
<td>0.2</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;0.05</td>
<td>5.0</td>
</tr>
<tr>
<td>pH</td>
<td>11.9</td>
<td>2.0–12.5</td>
</tr>
</tbody>
</table>


Mechanical Properties

Mechanical tests performed on stabilized FGD gypsum mixtures include moisture-density relations, unconfined compressive strength, dynamic modulus, and flexural fatigue. Discussed in the following sections of the paper will be the results of each individual test. Freeze-thaw, permeability, and triaxial data obtained on stabilized FGD gypsum mixtures can be found in other references (3,4).

Moisture-Density Relationships

Strength development in FGD mixtures can be achieved through stabilization with either Portland cement, fly ash, or combinations thereof. The optimum moisture content and maximum dry density values will be influenced by the method of compaction, the curing time, and the type and amount of stabilizers used (if any). Shown in Figure 1 are the moisture-density relationships for gypsum mixtures stabilized with 8 percent Type II cement and compacted in accordance with ASTM D1557—Method A (modified Proctor), ASTM D698 (standard Proctor) and Texas Method 113E. The Texas method specifies a compaction energy of 0.001 m-N/mm² (12.3 ft-lb/in²) and falls in between the two Proctor methods. The modified and standard Proctor compaction procedures yielded an optimum moisture content of 12 percent as compared with 14 percent moisture obtained using the Texas method. Higher maximum dry density values were obtained with the higher compaction energy levels.

Unconfined Compressive Strength Testing

After completing the compaction series, duplicate specimens were prepared at optimum moisture content for strength determination using the unconfined compression test (ASTM D1633). This method prescribes either a 101.6-mm (4-in.) diameter by 116.43-mm (4.584-in.) specimen—Method A (L/D = 1.15), or a 71.12-mm (2.8-in.) diameter by 142.24-mm (5.6-in.) specimen—Method B (L/D = 2). The former method was used because it was consistent with the modified Proctor compaction methodology. Molded specimens were cured in plastic bags before compression testing. The 7-day compressive strength results for cement stabilized gypsum mixtures prepared and compacted in accordance with the three compaction procedures previously described are shown in Figure 2. With an increase in cement content and compactive effort, there is an increase in the unconfined compressive strength.

Resilient Modulus Testing

The resilient modulus (M_r) is a dynamic test response defined as the ratio of the repeated axial deviator stress (s_d) to the recoverable axial strain (e_r). Test conditions (e.g., stress state, moisture content, compactive effort) affect M_r responses for different materials in different ways. The test is conducted in a triaxial device equipped for repetitive load conditions.

Resilient modulus testing was conducted on mixtures of FGD gypsum stabilized with 6 and 8 percent Type II cement. The specimens used were 101.6 mm (4 in.) in diameter by 203.2 mm (8 in.) high and were prepared so as to meet the compaction level set forth in ASTM D1557—Method A. The specimens were then wrapped in plastic bags and cured for 16 days at 23.3°C (74°F) and 100 percent relative humidity. Deformations were measured by using linear differential transformers (LVDTs) clamps bonded directly to the specimens. To minimize any extraneous deformation that may oc-
Typical results obtained from the resilient modulus testing on cement stabilized FGD gypsum mixtures are shown in Figures 3 and 4. The reason for using the high deviator stresses in those experiments is the difficulty encountered in getting any readings at the low stress levels. The resilient modulus for FGD gypsum stabilized with 6 percent Type II cement and tested at a bulk stress of 590 kPa (86 psi) is about 3,800,000 kPa (550,000 psi), whereas that mixture stabilized with 8 percent Type II cement and tested at the same bulk stress yielded a resilient modulus value of 12,000,000 kPa (1,750,000 psi). Such results are compared against different base materials in Figure 5. On the basis of the resilient modulus data, stabilized FGD gypsum blends should perform as well as any other conventional base materials in road base applications. However, the tensile strength data of cement stabilized FGD gypsum mixtures should be obtained and correlated with the resilient modulus data. If the resilient modulus of a stabilized material increases without a corresponding increase in tensile strength, it is likely to undergo tensile cracks.

**Flexural Fatigue Testing**

Research has demonstrated how shear strength in the pavement, flexural strength, and flexural fatigue life can be used to provide reliable acceptance criteria for the design of stabilized bases. In this study, flexural fatigue tests were used to develop a relationship between the unconfined compressive strength, the fatigue strength, and the resistance to low-temperature cracking.

Test specimens were prepared by compacting cement/FGD gypsum blends into 76.2 x 76.2 x 387.4-mm (3 x 3 x 15 1/14-in.) steel molds in two equal layers (6, 8, and 10 percent Type II cement were used in the preparation of the mixtures). The surface of the first layer was scarified before placement of the second layer to ensure bonding. Compaction was accomplished through a hammer with a 50.8-mm (2-in.) diameter base. The compactive effort was applied by a 44.5-N (10-lb)
weight free falling 457.2 mm (18 in.). Each layer received 75 blows to simulate the energy employed by ASTM D1557—Method A. The average dry density in the specimens was about 15.2 kN/m³ (97 lb/ft³). The specimens were then wrapped in plastic bags and placed in a curing room at 23.3°C (74°F) and 100 percent relative humidity. The samples were cured for 30 days. The length of cure was assumed to be representative of field conditions. After removal from the curing room, the specimens were tested at ambient room temperature and no attempt was made to control the temperature during the fatigue test.

The stress level in a fatigue test is commonly defined as the ratio of the applied stress to the static ultimate strength of the material. The flexural test specimens were tested under three-point loading and all samples were loaded at a constant rate of 1.27 mm/min (0.05 in/min) for measuring the static strength of the cement/FGD gypsum blends. Stress in the specimen was calculated assuming a constant cross-sectional area and a linear stress distribution. The loads in the dynamic test were applied at a rate of 720 cycles/min and the number of cycles to failure for each applied load was then recorded.

The results from the fatigue tests on the three mixtures are shown in Figures 6 and 7. It can be seen in Figure 6 that when the fatigue data are plotted as applied stress ($\sigma_{\text{applied}}$) versus the number of cycles to failure ($N_f$), a curve exists for each mix design. However, when the results are plotted as the ratio $\sigma_{\text{applied}} / \sigma_{\text{flexure}}$ as in Figure 7, all data can be presented by one curve. This ratio equals 0.60 at $N_f = 10^5$ cycles. Furthermore, it was shown from the static fatigue data that the flexural strength is approximately 0.2 times the unconfined compressive strength (UCS),

$$\sigma_{\text{flexure}} = (0.2) \text{(UCS)}$$

But

$$0.6 = \sigma_{\text{applied}} / \sigma_{\text{flexure}} \text{ at } N_f = 10^5 \text{ cycles}$$
Therefore

\[ 0.6 = \frac{\sigma_{\text{applied}}}{(0.2)} \text{ (UCS)} \]

or

\[ \text{UCS} = (8.5) (\sigma_{\text{applied}}) \]

This indicates that the compressive strength is of the order of 8.5 times the applied stress to cause failure in the road base. In a well-designed pavement system, this applied stress can be between 205 and 275 kPa (30 and 40 psi). On this basis, the design strength should be around 2050 kPa (300 psi) instead of the 4500 kPa (650 psi) strength that is normally required for base materials subjected to freeze-thaw cycles (Texas State Department of Highways and Public Transportation specifications). A demonstrated test fatigue life in excess of \(10^5\) cycles would be satisfactory for roads with low traffic volume, whereas \(10^8\) cycles would suffice for high traffic volumes. The latter would also demonstrate good resistance to low temperature as well as freeze-thaw cracking.

CONCLUSIONS

The results from the laboratory studies conducted on FGD gypsum warrant the following conclusions:

1. The radiological analysis indicates that FGD gypsum poses no risk if used as a road subbase-base material or in any other applications.
2. The results of the EP toxicity leachate tests indicate that fresh or stabilized FGD gypsum will meet the EPA Leachate Standards.
3. Compactive effort has a significant influence on the dry density and compressive strength of stabilized FGD gypsum mixtures.
4. Preliminary resilient modulus and flexural fatigue testing data indicate that stabilized FGD gypsum mixtures should perform satisfactorily as road base and subbase materials.

RECOMMENDATIONS

Further laboratory testing is needed to evaluate the properties of stabilized and unstabilized FGD gypsum mixtures. Wet-dry, expansion, tensile strength, and water submersion data should be obtained on these mixtures. Furthermore, the leachate analysis should be conducted using the Toxicity Characteristic Leaching Procedure.

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REFERENCES