

Environmental Characteristics of By-Product Gypsum

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A family of by-product gypsum materials—such as flue gas desulfurization (FGD) gypsum, phosphogypsum (PG), fluorogypsum, titanogypsum, and disulfogypsum—is produced as a result of stringent environmental regulations or are inherent to the industrial processes themselves. From a mineralogical viewpoint, all these materials are calcium sulfate. However, they are produced as a result of different industrial processes. About 18 million Mg (20 million tons) of FGD gypsum and 54 million Mg (60 million tons) of PG are generated annually in the United States. Current stockpiled quantities of FGD gypsum and PG are about 136 and 726 million Mg (150 and 800 million tons), respectively. One major application for the use of these materials is in road base and subbase construction. Phosphogypsum, a by-product of phosphoric acid production, was investigated for the past 20 years in Florida, Louisiana, and Texas. However, as a result of the 1989 Environmental Protection Agency (EPA) regulations related to the disposal of phosphogypsum, limited research is being conducted on this material. FGD gypsum, a by-product of sulfur oxides emission control systems, is still being evaluated. Fluorogypsum, a coproduct of the production of hydrogen fluoride, is being successfully marketed as a base and subbase material in the Houston, Texas, area. There is little information about the use of titanogypsum and disulfogypsum. A summary of the mineralogical, morphological, physical, chemical, radiological, and leachate characteristics of PG, FGD gypsum, and fluorogypsum is presented. Where applicable, properties of these materials will be compared with EPA environmental standards.

Geographic shortages of quality construction materials, rising transportation costs, and increasing environmental awareness have spurred the need to develop more cost-effective construction methods and materials. Wastes and by-products generated by industry are among the materials currently receiving attention as partial or full replacement for aggregates. Many by-products are generated as a result of stringent environmental regulations or are inherent to the industrial processes themselves. In either case, the main obstacles for by-product reuse are economic and environmental. For the past 20 years, considerable work was conducted on a family of by-product gypsum materials, including flue gas desulfurization (FGD) gypsum, phosphogypsum (PG), and fluorogypsum.

FGD gypsum is a by-product of the recovery of sulfur oxides from the flue gases generated at power plants that burn coal. A natural contaminant of coal, sulfur is almost completely converted to sulfur oxide (SO_x) when coal is burned. FGD processes result in SO_x removal by inducing exhaust gases to react with a chemical absorbent as they move through a scrubber (1). 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 or stabilized with fly ash before stockpiling, this material consists predominantly of either calcium sulfite (CaSO_3) or calcium sulfate (CaSO_4) crystals. The latter is preferred for disposal and use. Excess air must be provided to the process to convert the scrubber residual to calcium sulfate. It has been estimated that 18 million Mg (20 million tons) of FGD gypsum are generated annually in the United States and has already created an inventory of 136 million Mg (150 million tons). It has been projected that this inventory will quadruple in 40 years (M. Golden, Electric Power Research Institute, personal communication).

Phosphogypsum is a solid by-product of wet process phosphoric acid production. Generally, finely ground phosphate rock, $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$, 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 (2). The resulting filter cake containing the hydrated calcium sulfate is called phosphogypsum. As a general rule, 4 to 5 Mg (4.5 to 5.5 tons) of PG are produced for every ton of phosphoric acid produced (3). In the United States, phosphogypsum is currently being produced at a rate of 54 million Mg (60 million tons) per year. Long-term projections indicate that more than 1.4 billion Mg (1.54 billion tons) will be stockpiled in Florida, Louisiana, and Texas by 2000 (4).

Fluorogypsum is a coproduct of the production of hydrogen fluoride (HF). In the process, fluorspar (calcium fluoride) reacts with condensing sulfuric acid (H_2SO_4) to form HF gas and calcium sulfate. The reacted fluorspar leaves the reactor as solid calcium sulfate and is pumped into a slurry tank where it is neutralized with lime and then pumped to settling ponds for storage (5).

As stockpiles continue to grow and environmental constraints become more stringent, widespread uses of by-product gypsum materials must be developed. One possible large-volume application for the use of these materials is in road base and subbase construction.

MATERIALS

FGD Gypsum

The FGD gypsum used in this study came from the Texas Utilities-Electric Sandow Power Station at the Alcoa Plant in Rockdale, Texas. The material consists mainly of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) crystals.

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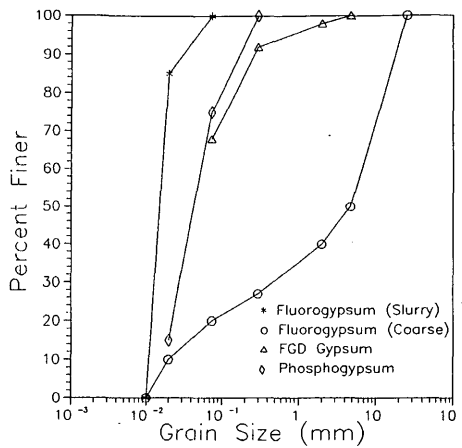


FIGURE 1 Typical grain size distribution curves for FGD gypsum, fluorogypsum, and phosphogypsum.

Phosphogypsum

The phosphogypsum used in the research program was collected from stockpiles at the Uncle Sam Plant of the Agrico Chemical Company in Louisiana. The company uses the dihydrate modification of the wet process to produce phosphate fertilizers. Therefore, the phosphogypsum crystals are in the dihydrate form ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Fluorogypsum

Fluorogypsum is generated at the E.I. DuPont De Nemours & Company, Inc., HF Plant in LaPorte, Texas. The material is initially produced in the anhydrite form (CaSO_4). However, after neutralization with a lime slurry, the fluorogypsum will be converted primarily to the dihydrate form.

EXPERIMENTAL INVESTIGATION

The Texas Transportation Institute (TTI) at Texas A&M University, the Institute for Recyclable Materials (IRM) at Louisiana State University, and the Florida Institute of Phosphate Research (FIPR) at Bartow, Florida, took the lead in investigating the potential use of by-product gypsum materials. Laboratory and field studies were conducted to establish the potential use of these materials in high-

way construction as well as other applications. This paper presents a summary of the mineralogical, morphological, physical, chemical, radiological, and leachate characteristics of phosphogypsum, FGD gypsum, and fluorogypsum.

Mineralogical and Morphological Characteristics

Mineralogical testing indicated the phosphogypsum, FGD gypsum, and fluorogypsum crystals are mainly calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with the presence of other minor elements. Morphological testing was conducted using optical and scanning electron microscopy (SEM). By-product gypsum particles are generally radiating agglomerates of platelets. Some of the aged or weathered materials tend to be denser.

Physical Properties

FGD gypsum, phosphogypsum, and fluorogypsum are nonplastic materials consisting primarily of particles ranging in size from fine sand to silt. Based on the Unified Soil Classification System (USCS), these materials would be classified as ML. However, because of cementation, fluorogypsum samples excavated from the settling ponds tend to have coarser particle sizes. Figure 1 shows typical grain size curves for FGD gypsum, phosphogypsum, and fluorogypsum. The physical properties of these materials are listed in Table 1. Free moisture in the materials can be obtained by drying the samples at temperatures below 55°C (131°F). At temperatures above 70°C (158°F), all chemically or structurally bonded water will also be removed. This temperature regime is not sufficiently high to cause gypsum roasting, a phenomenon that would change the physico-chemical characteristics of the material. Results (6) show that gypsum roasting occurs only at temperatures on the order of 800°C to 1000°C ($1,472^\circ\text{F}$ to $1,832^\circ\text{F}$).

Chemical Properties

The chemical analysis of the three by-product gypsum materials is presented in Table 2. The materials consist mainly of calcium (Ca) and sulfate (SO_4) crystals. Also, a number of trace elements are present in FGD gypsum, phosphogypsum, and fluorogypsum. Typical concentrations of these elements are presented in Table 3. With the exception of the lead (Pb) concentration in phosphogypsum, the concentrations of the leachable metals from the three fresh by-product gypsum materials are well below the Environmental Protection Agency (EPA) leachate standards.

TABLE 1 Results of Physical Analyses of By-product Gypsum Materials

Property	FGD Gypsum ^a	Phosphogypsum	Fluorogypsum
Free Moisture (%)	14	8-18	5-30
Structural Moisture (%)	26	25-30	NA ^b
Specific Gravity	2.30	2.35	2.96

^aAverage of 90 Samples.

^bNA = Not Available.

TABLE 2 Results of Chemical Analyses of By-product Gypsum Materials

Constituent Content	FGD Gypsum (%)	Phosphogypsum (%)	Fluorogypsum (%)
CaO	24.0	29-31	29.0
SO ₄	54.0	50-53	42.1
SiO ₂	2.7	5-10	0.5
CO ₃	3.0	NA	NA
F	NA ^a	0.3-1.0	NA
P ₂ O ₅	NA	0.7-1.3	NA
Fe ₂ O ₃	NA	0.1-0.2	0.2
Al ₂ O ₃	NA	0.1-0.3	0.08
pH	7.0	2.8-5.0	11-12

^aNA = Not Available.

Radiological Testing

A radiological evaluation was conducted on 12 samples of FGD gypsum. The average Radium-226 content was about 0.92 pCi/g. This concentration is in the same range values (0.3 to 5.3 pCi/g) for cement (8). There is no radioactivity associated with fluorogypsum. The average Radium-226 concentration in the Louisiana phosphogypsum is about 29 pCi/g (Scott and Zhang, unpublished data). The source of this radioactivity is the natural phosphate rock that contains approximately 45 microcuries/ton of Radium-226. In the Florida and Louisiana cases, the phosphoric acid is produced using phosphate rock mined in central and southern Florida. In the wet process of manufacturing phosphoric acid, most of the Radium-226 is not dissolved by acidulation with sulfuric acid and thus remains with the phosphogypsum.

Radon emanation studies are currently underway at the Institute for Recyclable Materials (Zhang, unpublished data). These

studies encompass theoretical predictions and experimental measurements of radon emanation from raw and cement-stabilized phosphogypsum. For 203.2 mm (8-in.) thick specimens, the results of these studies have indicated emanation rates of 10 pCi/m²/sec or lower for various combinations of cement content, relative compaction, compaction water content, degree of saturation, type and content of admixture, and curing time. EPA emission standards for radon emissions from phosphogypsum stacks limit flux to no more than 20 pCi/m²/sec. (A complete summary of the results of this study will be reported in a future paper.)

Leachate Testing

This section presents laboratory as well as field leachate data generated on phosphogypsum and FGD gypsum.

TABLE 3 Typical Trace Element Concentrations in By-product Gypsum Materials

Element	FGD Gypsum (mg/l)	Phosphogypsum (mg/l)	Fluorogypsum (mg/l)	USEPA TCLP (mg/l)	USEPA Drink. Water (mg/l)
As	< 0.01	1-5	ND ^b	5.0	0.05
Ba	< 0.50	50	Trace	100	1.0
Cd	< 0.01	0.3-0.4	NA	1.0	0.01
Cr	< 0.05	2-5	0.001	5.0	0.05
Pb	< 0.05	2-10	0.04	5.0	0.005
Hg	< 0.001	0.02-0.05	0.13	0.2	0.002
Se	< 0.01	1	NA	1.0	0.01
Ag	< 0.05	0.1-0.2	NA	5.0	0.05
SO ₄ (%)	18.84	NA ^a	NA	NR ^c	0.03

^aNA = Not Available.

^bND = Not Detected.

^cNR = Not Required.

TABLE 4 Leachate Characteristics of Materials Used on 1992 Roadway Demonstration Project at Texas A&M University Riverside Campus (9)

Elem.	FGD Gypsum (mg/l)	Dry Bottom Ash (mg/l)	Wet Bottom Ash (mg/l)	Cement (mg/l)	Job Mix (mg/l)	USEPA TCLP (mg/l)	EPA Drink. Water (mg/l)
As	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	5.0	0.05
Ba	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	100	1.0
Cd	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.0	0.01
Cr	< 0.05	< 0.05	< 0.05	0.125	< 0.05	5.0	0.05
Pb	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	5.0	0.005
Hg	< 0.001	< 0.001	< 0.001	< 0.001	< .001	0.2	0.002
Se	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.0	0.01
Ag	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	5.0	0.05
SO ₄ (%)	18.84	0.055	0.095	1.48	10.95	NR ^a	0.03

^aNR = Not Required.

Laboratory Leachate Testing

On the basis of the toxicity characteristic leaching procedure (TCLP) test, IRM conducted a comprehensive study of the leachability of raw and cement-stabilized phosphogypsum (Thimmegowda, unpublished data). This study encompassed four different types of cement, two levels of relative compaction, and two cement contents. The results generally indicated that the leachability of cement-stabilized phosphogypsum was not significantly affected by relative compaction but that both cement content and type did produce a measurable effect. In general, chromium and barium leached in increased amounts compared to raw phosphogypsum. These increased amounts were attributed to the higher natural levels of these metals in the cements. However, in no case did the concentrations of the leached metals exceed EPA leachate standards.

Field Leachate Testing

In 1991 and 1992, two demonstration roadway projects using FGD gypsum were constructed at the Texas A&M Riverside Campus 24.2 km (15 mi) from the main campus. The 1991 road section was a two-lane, 91.5-m (300-ft) long test section. The pavement cross section consisted of 203.2 mm (8 in.) of FGD gypsum stabilized with 7 percent by dry weight of a high-sulfate-resistant cement. A Type D surface treatment was then placed over the base. The 1992 roadway project was identical to the 1991 test section. However, in this project, wet bottom ash (boiler slag) and dry bottom ash (cinder ash) were added to the stabilized FGD gypsum mixtures as coarse fractions to improve their compacted density (9). The mixture design for the 1992 section consisted of 50 percent by weight FGD gypsum, 50 percent by weight bottom ash (75 percent of which is wet bottom ash and 25 percent is dry bottom ash), and 7 percent by dry weight high-sulfate-resistant cement.

Laboratory analyses of the five materials used in the 1992 roadway section were conducted for leachable metals and sulfates. Leachates were evaluated by means of equilibrium batch extraction and slurry techniques. The results are shown in Table 4 (10). The

materials were extracted at solid:solution ratios of 1:5, 1:20, and 1:100 for 24- and 72-hr equilibration times. EPA TCLP protocol requires a 1:20 acidic extraction for 18 hr. Values from leachate tests for the 1992 job mix do not approach the maximum allowable limits for TCLP. Most of the metals were below the instrument detection limits.

To measure subsurface migration of chemical constituents during construction and weathering of the test pavement, six vacuum extraction soil moisture cups were used (see Figure 2). The cups were installed in the unsaturated zone 3.05 m (10 ft) below the surface. They were positioned in the drainage ditches on each side of

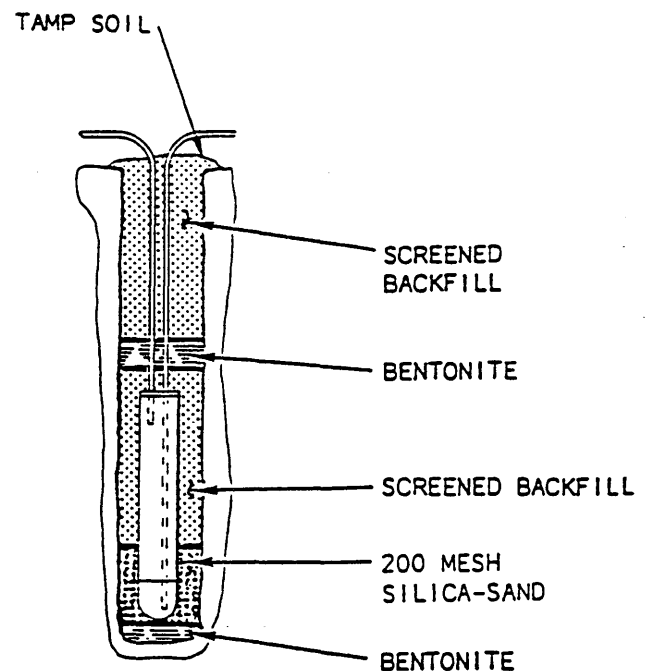


FIGURE 2 Vacuum extraction soil moisture cup (9).

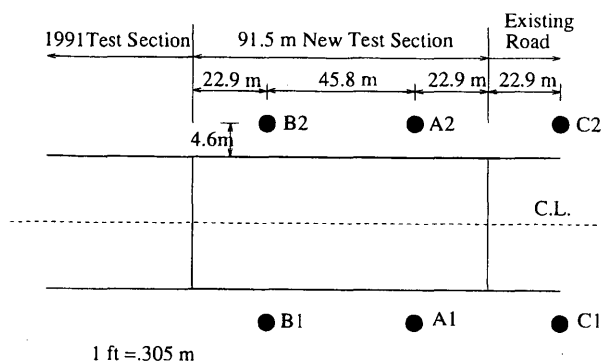


FIGURE 3 Location of soil moisture collection cups (9).

the roadway about 4.6 m (15 ft) from the roadbed with a distance of 45.8 m (150 ft) between collection sites (see Figure 3). Sites A and B are located on the 1992 test section. Site C is located on the existing road 22.9 m (75 ft) from the experimental road to serve as a background sample for reference. A vacuum pressure of negative 60 centibars was applied to each moisture cup (10).

Water samples were collected from the surface and the soil moisture cups in November 1992 (0 months), February 1993 (3 months), January 1994 (9 months), and July 1994 (18 months). The test results for surface water and leachate analyses are presented in Tables 5 and 6 (10).

The surface water collected from the drainage ditches passes EPA drinking water standards for all metals, except lead. However,

the lead content is still much lower than the TCLP requirement of less than 5 mg/L. The total dissolved solids (TDS) for site C1 are 2556 mg/L, which is high for the drinking water standards, but over 5000 mg/L is acceptable for agricultural or runoff purposes. Water samples collected from sites C1 and A1 indicate that there is very little difference between the two sections. The water contains low metal concentrations and is below allowable EPA drinking water standards. Table 6 indicates that sulfates concentration has increased from 3 mg/L at 3 months to 82 mg/L after 15 months. However, such concentration is still well below EPA drinking water standard of 250 mg/L. On the basis of the results presented, there was no adverse environmental impact created by the FGD gypsum and bottom ash road test section.

CONCLUSIONS

From an environmental perspective, the following conclusions are warranted about the environmental concerns associated with the use of by-product gypsum materials in road base and subbase construction:

- Unmodified or stabilized FGD gypsum poses a negligible environmental impact, except for areas that could affect drinking water. The main area of concern is sulfate concentration. This conclusion is also true for the use of raw or stabilized fluorogypsum in road base applications.
- The main issue of the use of phosphogypsum is the uncertainty about the possible health effects related to radon emanation from

TABLE 5 Surface Water Analysis of FGD Gypsum and Bottom Ash (1992 Test Section)

Element	11/92 (mg/l)	2/93 (mg/l)	1/94 (mg/l)	7/94 (mg/l)	USEPA TCLP (mg/l)	USEPA Drink. Water (mg/l)
As	< 0.01	< 0.01	< 0.01	< 0.01	5.0	0.05
Ba	< 0.50	< 0.50	< 0.50	< 0.50	100.0	1.0
Cd	< 0.01	< 0.01	< 0.01	< 0.01	1.0	0.01
Cr	< 0.05	< 0.05	< 0.05	< 0.05	5.0	0.05
Pb	0.38	< 0.05	0.03	< 0.41	5.0	0.005
Hg	< 0.001	< 0.001	< 0.001	< 0.001	0.2	0.002
Se	< 0.01	< 0.01	< 0.01	< 0.01	1.0	0.01
Ag	NA ^b	< 0.05	NA	NA	5.0	0.05
Al	NA	< 0.05	< 0.08	< 0.05	NR ^c	0.20
Cu	NA	< 0.05	< 0.05	< 0.05	NR	NR
Fe	NA	0.18	< 0.001	< 0.001	NR	0.30
Mn	NA	0.04	< 0.0002	< 0.0012	NR	0.05
Zn	NA	1.92	1.90	1.87	NR	5.0
SO ₄	0.9	1.20	0.80	0.7	NR	250
TDS ^a	45.5	54.60	209	48.0	NR	500

^aTDS = Total Dissolved Solids.

^bNA = Not Available.

^cNR = Not Required.

TABLE 6 Soil Leachate Analysis of FGD Gypsum and Bottom Ash (1992 Test Section)

Element	11/92 (mg/l)	2/93 (mg/l)	1/94 (mg/l)	7/94 (mg/l)	USEPA TCLP (mg/l)	USEPA Drink. Water (mg/l)
As	< 0.01	< 0.01	< 0.01	< 0.01	5.0	0.05
Ba	< 0.50	< 0.50	< 0.17	< 0.50	100.0	1.0
Cd	< 0.01	< 0.01	< 0.002	< 0.01	1.0	0.01
Cr	< 0.05	< 0.05	< 0.003	< 0.05	5.0	0.05
Pb	< 0.05	< 0.05	0.025	< 0.05	5.0	0.005
Hg	< 0.001	< 0.001	< 0.002	< 0.001	0.2	0.002
Se	< 0.01	< 0.01	< 0.01	< 0.01	1.0	0.01
Ag	< 0.05	< 0.05	0.023	< 0.05	5.0	0.05
Al	< 0.05	< 0.05	< 0.16	< 0.05	NR ^c	0.20
Cu	NA ^b	NA	NA	NA	NR	NR
Fe	< 0.04	0.18	< 0.017	< 0.19	NR	0.30
Mn	0.03	0.02	0.009	0.009	NR	0.05
Zn	0.024	0.026	0.007	0.009	NR	5.0
SO ₄	0.81	2.98	81.6	7.2	NR	250
TDS ^a	256	Trace	396	Trace	NR	500

^aTDS = Total Dissolved Solids.

^bNA = Not Available.

^cNR = Not Required.

this material. Further studies must be directed at an improved understanding of the health-related risks associated with raw or stabilized phosphogypsum. The studies must consider the short-term exposure to construction workers and the long-term exposure to users of such facilities. In addition, further studies to assess the factors influencing the radon emanation rate are warranted. Sulfate concentration could be another area of concern where the quality of drinking water is important.

ACKNOWLEDGMENT

The authors thank M. Larry Schwarz of E.I. DuPont De Nemours & Company, Inc., for providing the data about fluorogypsum.

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Publication of this paper sponsored by Committee on Cementitious Stabilization.