Pergamon

Cement and Concrete Research, Vol. 26, No. 7, pp. 1083-1094, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in the USA. All rights reserved
0008-8846/96 $15.00 + .00

PII S0008-8846(96)00083-X

THE INFLUENCE OF ADMIXTURES ON THE STRENGTH AND LINEAR EXPANSION OF CEMENT-STABILIZED PHOSPHOGYPSUM

C.S. Gutti, A. Roy, J.B. Metcalf and R.K. Seals
Institute for Recylable Materials, Louisiana State University,
Baton Rouge, LA 70803

(Refereed)
(Received February 26, 1996; in final form April 21, 1996)

ABSTRACT

The effect of admixture content, dry density and curing condition on linear expansion of cement-stabilized phosphogypsum (CSPG) was studied over a ninety-day period. The phosphogypsum was stabilized using 8% Type I portland cement. Cylindrical CSPG specimens (51mm X 102 mm) were fabricated by static compaction (ASTM D 698) at three density levels: standard Proctor maximum dry density (13.7 kN/m^3) and 5% on either side of this density with a moisture content (20%) corresponding to the maximum standard Proctor dry density. $CaCl_2$ (1% and 2 %) and Daraset (0.05% and 0.15%) as a percentage of the amount of cement, were added to CSPG. Curing conditions were (at ambient temperature): open to air, moisture-controlled and soaked. Selected specimens were analyzed by derivative thermogravimetry and scanning electron microscopy.

When cured under moisture-controlled environment, CSPG had a short initial period of expansion irrespective of the dry density or admixture content. Increasing dry density led to a period of contraction following expansion. At the same dry density, the additon of $CaCl_2$ led to a period of no length change while the addition of Daraset led to more initial expansion. The length change, over time, of air-cured CSPG specimens was negligible. The correlation between ettringite content and expansion was crude. For soaked specimens, ettringite growth was widespread and unusually high. Compacted at the lowest density (13.0 kN/m^3) and cured in moisture-rich environments, CSPG deteriorated significantly.

Introduction

Phosphogypsum (PG) is a solid by-product of the manufacture of phosphoric acid by the wet-process. PG unsually consists of tabular, interlocking crystals. The median diameter of the individual PG crystals is 62 micrometers, with 90% falling between 16 and 206 micrometers (1). Based on the grain-size distribution and American Association of State Highway and Transportation Officials (AASHTO) soil classification system, PG is classified as a silty soil (2). Mineralogically, PG ($CaSO_4.2H_2O$) is identical to natural gypsum but is different from the latter in that it contains impurities such as water-soluble fluoride and P_2O_5, P_2O_5 substituted in the gypsum crystal lattice (3), and tens of ppm of toxic elements like As, Sb, etc (4). Depending on the source of the ore, PG also contains varying levels of the radioactive element ^{226}Ra (ca. 20 pci/g for Florida PG) (5). The projected amount of PG stock piled in Florida alone by the year 2000 A.D. is a billion tons.

However, PG has poor drainage characteristics, low unconfined compressive strength (UCS) and poor durability when subjected to mechanical stabilization only. Stabilization of PG with portland cement (cement-stabilized phosphogypsum (CSPG)), has been demonstrated to improve these properties (1,6,7,8).

Cement-stabilized soils for road-base construction requires a certain minimum unconfined compressive strength (9). The requirement for the Louisiana Department of Transportation and Development is 1.7 MPa (250 psi) after 7 days. Research studies conducted at the Institute for Recyclable Materials (IRM), Louisiana State University, demonstrated that PG stabilized with 14% cement by dry weight or more and compacted at standard Proctor maximum levels, can achieve minimum strength requirements (10). Even though this is less than an equal percentage in soil because of the low specific gravity of the PG (ca. 2.3), the use of that much cement makes CSPG less attractive economically for road base construction. The early strength can also be increased by adding chemical admixtures (11) such as $CaCl_2$. An earlier study at IRM suggested that $CaCl_2$ can indeed increase the 7-day strength (12). However, admixtures are also known to influence volume change characteristics of soils (11).

Volume changes in bases and subbases also influence the durability of the pavement structure. Heave in CSPG mixtures was reported in two field applications in Texas. Severe distress in pavements was observed after 122 days in LaPorte, Texas (13), and after one year in a parking lot constructed using CSPG in Houston (14). The causes for the distress were attributed to high moisture contents and low densities of the CSPG base.

The objective of this study was to investigate the effect of admixtures on the linear expansion of CSPG with 8% Type I portland cement. The admixtures were calcium chloride and Daraset, added at different concentrations. The influence of admixture concentration, dry density, and curing conditions on the linear expansion of CSPG was investigated. In addition, mineralogical and microstructural characteristics of CSPG were studied to see if length change could be correlated to these properties.

Materials and Methods

The materials utilized in the study were phosphogypsum, Type I portland cement, and Type C admixtures $CaCl_2$ and Daraset (a non-corrosive, non-chloride admixture). The PG used in this study came from the Uncle Sam Plant of Freeport McMoRan, Inc., in Louisiana. CSPG specimens, 51mm (2") in diameter and 102 mm (4") long cylinders, were formed by static compaction (ASTM D 698) for the expansion tests. PG was stabilized with 8% (by weight of PG) Type I portland cement. Specimens were fabricated at three different density levels: standard Proctor maximum dry density (13.7 kN/m^3 (87 pcf)) and 5% on either side of this density. A moisture content (20%) corresponding to the maximum standard Proctor dry density was used for all specimens. $CaCl_2$ was added at 1% and 2 % and Daraset was added at 0.05% and 0.15% concentrations to CSPG as a percentage of the amount of cement.

Curing was accomplished under three conditions: open to ambient conditions; moisture-controlled; and soaked. Moisture-controlled specimens were cured in air-tight plastic (ziploc) bags and soaked specimens were cured by immersing (after 7 days of moisture-controlled curing) the specimens completely in water.

Measurements for length change (ASTM C 490) were made using a comparator with a precision of 0.025 mm (0.0001 inch). The length of the specimens was recorded after 1, 3, 7, 14, 21, 30, 50, 60, 75 and 90 days. The data were used to calculate percentage change in length relative to the original length. Length change of the soaked CSPG specimens could not be measured because the bearings could not be placed on the wet cylindrical specimens.

Selected specimens were analyzed by derivative thermogravimetry (DTG) and scanning electron microscopy (SEM). DTG analysis was used to quantify the amount of ettringite, the amount of PG that has reacted and the amounts of calcium hydroxide and calcium carbonate present in a CSPG specimen.

The DTG runs were made from 25°C to 1000°C with the following steps: i) 25°C to 40°C at 5°C/min; ii) held for 10 min at 40°C; iii) 40°C to 200°C at 5°C/min; and iv) 200°C to 1000°C at 10°C min, using a Seiko TA 220 Thermal Analyzer. Nitrogen was used as the purge gas. The samples were not oven-dried or otherwise treated because trial runs suggested that ettringite and other hydrated phases will decompose by 105°C. The samples were analyzed immediately after grinding. The amount of sample ranged from 15 to 25 mg. The weights of calcium hydroxide, calcium carbonate and PG obtained from DTG are normalized to the weight of the sample at 40°C where it was held for 10 min to remove the moisture. The peak areas were determined using Peakfit™ from Jandel Scientific Software. Scanning electron microscopy was performed with a Cambridgescan S-260 microscope. The operating voltage was usually 20 keV. Specimens were prepared for SEM by freeze-fracturing in liquid nitrogen.

Results

Linear Expansion. FIG. 1 shows the effect of $CaCl_2$ on the expansion of CSPG specimens in a moisture-controlled environment at the same dry density. After expansion for about 15 days there was a net shrinkage in the absence of any $CaCl_2$ for the remainder of the experiment but when the admixture was added there was very little change in length over time, if any. The curve for 1% $CaCl_2$ has a similar shape as that without any admixture except that it has more initial expansion. The addition of Daraset produced more expansion (ca. 20-50% greater than control) for the first 20 days or so, which was followed by slight shrinkage and then no change (FIG. 2). The addition of Daraset magnified the effect seen on the length change curve in the absence of any admixture.

FIG. 3 shows the expansion in CSPG for different dry densities cured under moisture-controlled conditions. There was a short initial period of expansion at all dry densities. At the higher density ($\geq$ 14.3 kN/m^3 (91pcf)) there was some shrinkage beyond the first few weeks, followed by essentially no length change; whereas, at 13 kN/m^3 (83 pcf), some slight expansion continued up to 90 days.

In summary, moisture controlled curing led to an initial period of rapid expansion followed by little or no subsequent expansion (FIG. 3). Most of the expansion occurred within the first 25 days. Air-cured specimens, in contrast, showed very little length change over the period of study. Though length changes of soaked CSPG could not be measured, several changes in the specimens were observed. By the eighth week of curing, specimens with lowest density showed spalling (FIG. 5). By the thirteenth week, deep cracks extended through several of these specimens.

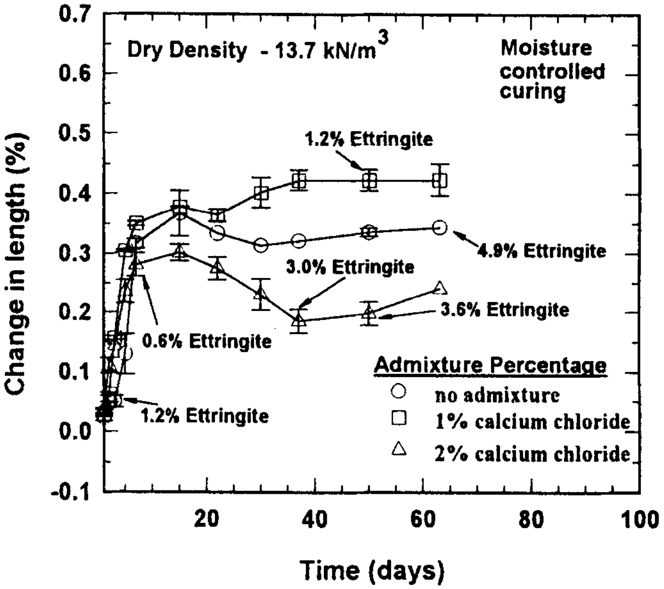

FIG. 1.
Relationship between calcium chloride concentration and length change in CSPG.

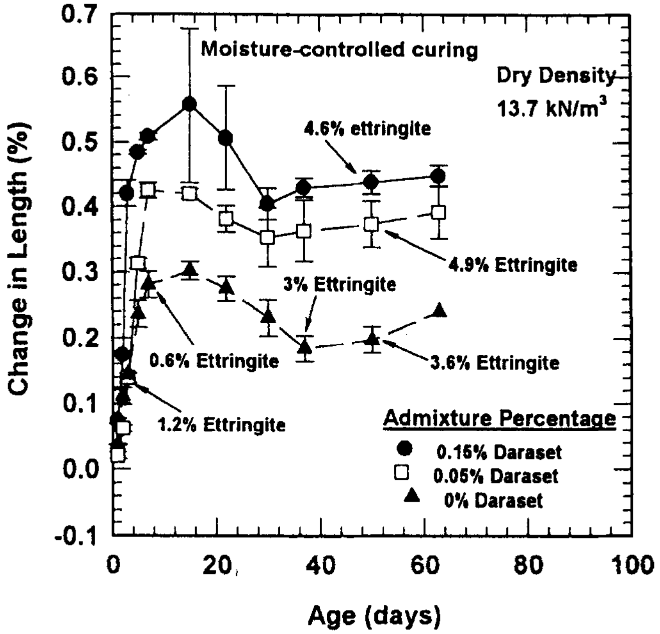

FIG. 2.
Relationship between Daraset concentration and length change in CSPG.

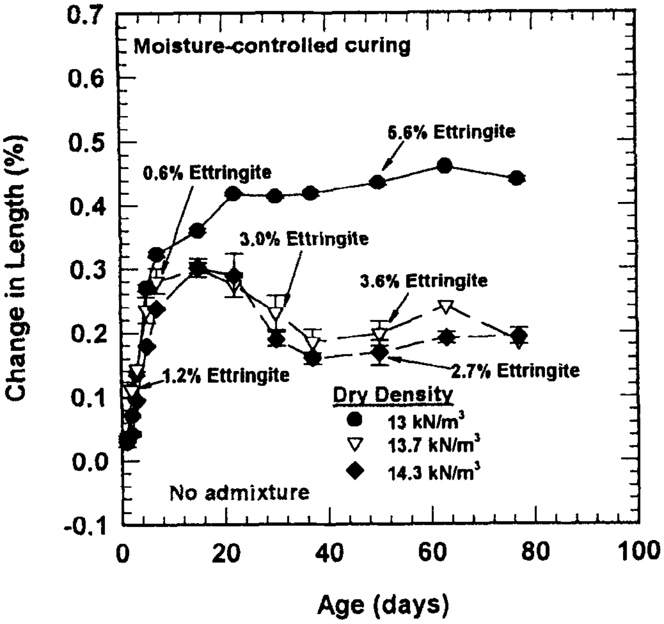

FIG. 3.
Influence of dry density on length change in CSPG.

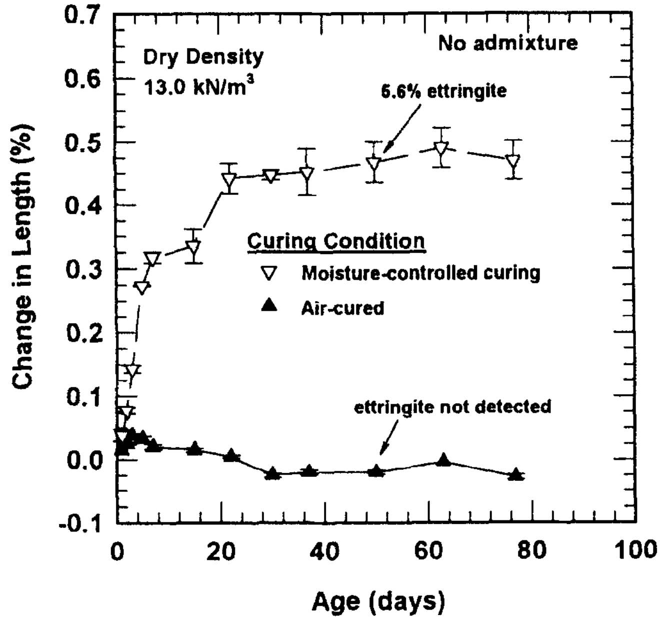

FIG. 4.
Influence of curing conditions on length change in CSPG.

Mineralogy of CSPG. The presence of ettringite, PG, calcium carbonate and calcium hydroxide was investigated in selected CSPG specimens based on DTG anlaysis. In general, the following peaks were found in the DTG curve of a CSPG specimen:

The effect of admixtures on the mineralogy of CSPG specimens is shown in Tables 2 and 3. FIG. 1 and FIG. 2 also show the variation in ettringite content with admixture concentration. For soaked curing, at the same moisture content and dry density, the amount of ettringite decreased with increasing $CaCl_2$ content (Table 2). There was also a significant decrease in PG content at the lowest admixture content. When cured under a moisture-controlled condition, for the same dry density, the amount of ettringite increased with increasing Daraset content but the change in PG content was insignificant (Table 3).

The effect of dry density on the mineralogy of CSPG cured under moisture-controlled conditions is shown in Tables 3 and 4. FIG. 3 also shows the variation in ettringite content with varying dry density. Ettringite was not detected in air-cured specimens at any dry density. For the other two curing regimes, increasing dry density led to less ettringite. There was a substantial loss of PG except at the highest dry density. The amount of calcium carbonate also increased with increasing dry density.

Tables 3 and 4 show the effect of curing condition on phase composition of CSPG. For the same dry density, ettringite was not detected in air-cured specimens, was conspicuous in moisture-controlled specimens and increased in amount with soaked curing. At the same dry density (13.0 kN/m3), very little PG was lost from the air-cured specimens, increased slightly for the moisture-controlled curing and was substantial with soaked curing (Table 4).

Microstructure of CSPG. Some of the eight-week-old CSPG specimens compacted at the lowest dry density and cured under water showed evidence of failure in the form of spalling (FIG. 5). The mineralogy of the specimens, analyzed by DTG, showed high ettringite content and dissolution (loss) of greater amounts of PG. Therefore, the microstructure of soaked CSPG was studied using the SEM in order to find a possible explanation for this behavior. The microstructure of three specimens of these samples was studied. One specimen was obtained from a cylinder which did not fail. Two others were obtained from the interior and the spalled surface, respectively, of a specimen showing failure.

CSPG consisted of aggregates of PG crystals of varying size (FIG. 6). At low magnifications (tens to a few hundreds X), the PG crystals could be easily identified by their tabular morphology and smooth crystal faces. At this magnification, the distribution of the binding phase was heterogenous. The clumps of PG crystals often had very little cement in

TABLE 1
Identification of DTG Peaks

Temperature range	**Phase**
50-75 °C	ettringite
100-125 °C	gypsum
210-250 °C	This peak was usually found in most runs, independent of curing condition, dry density or the presence or absence of admixture. The peak could be due to some aluminate phase which is usually found in this temperature range in DTG.
414°C	calcium hydroxide
570-650 °C	calcium carbonate

TABLE 2
Mineralogy of Fifty-Day Old Soaked CSPG for Different Admixture Concentrations*

Admixture	Admixture Amount (%)	Ettringite (%)	PG (%)	Calcium Carbonate (%)
CaCl2	0	4.0	66	1.5
CaCl2	1	3.7	84	0.4
CaCl2	2	2.4	84	2.3

* (Moisture Content = 20% and Dry Density = 13.7 kN/m3)

between them. At higher magnifications (thousands X), some PG crystals showed extensive dissolution (FIG. 7).

The cement matrix with abundant ettringite needles was more clearly seen at magnifications of several hundred times and up. The ettringite needles could be broadly divided into two types based on their length and morphology: the large ones, as much as five micrometers long with well-defined crystal faces, and the smaller sub-micrometer-sized ones with poorly defined crystal faces (15). The larger crystals sometimes grew together as radiating spherules (FIG. 8). The smaller crystals formed a sub-micrometer-thick felt-like layer on the surface of the PG crystals. Though these two morphologies usually occurred together, in some regions only the larger ettringite crystals were present.

TABLE 3
Effect of Curing condition, Dry Density and Admixture Concentration on Phase Proportions in Fifty-Day Old CSPG

Curing Condition	Dry Density (kN/m3)	Admixture	Admixture Amount (%)	Ettringite (%)	PG (%)	Calcium Carbonate (%)
air-dried	13.0	None	0	n.d.	87.0	1.3
Moisture controlled (Moisture content=20%)	13.0	None	0	5.7	82.6	0.4
	13.7	None	0	2.4	80.0	0.2
	14.3	None	0	2.7	81.3	0.4
	13.7	CaCl2	0	2.4	80.0	0.2
	13.7	CaCl2	1	3.6	83.7	0.1
	13.7	CaCl2	2	1.2	76.0	2.3
	13.7	Daraset	0	2.4	80.0	0.2
	13.7	Daraset	0.05	4.9	78.0	0.2
	13.7	Daraset	0.15	4.7	80.0	0.2
Soaked curing	13.0	None	0	6.7	65	0.5
	13.7	None	0	4.0	66	1.5
	14.3	None	0	4.0	85	1.7

TABLE 4
Ettringite Content of Fifty-Day Old CSPG for Different Dry Densities*

Dry Density (kN/m3)	% ettringite present in specimens		
	curing condition		
	air-cured	moisture-controlled	soaked
13	n.d	5.7	6.7
13.7	n.d.	2.4	4.0
14.3	n.d.	2.7	4.0

*(Moisture Content = 20%); n.d. = not detected.

These larger ettringite crystals were sometimes seen protruding out of PG grains (FIG. 6). Ettringite growth was also seen on PG grains present as clumps distant from any calcium silicate hydrate. No significant or apparent microstructural difference was observed between the spalled surface and the interior of the failed specimen, or between these and the specimen that did not fail.

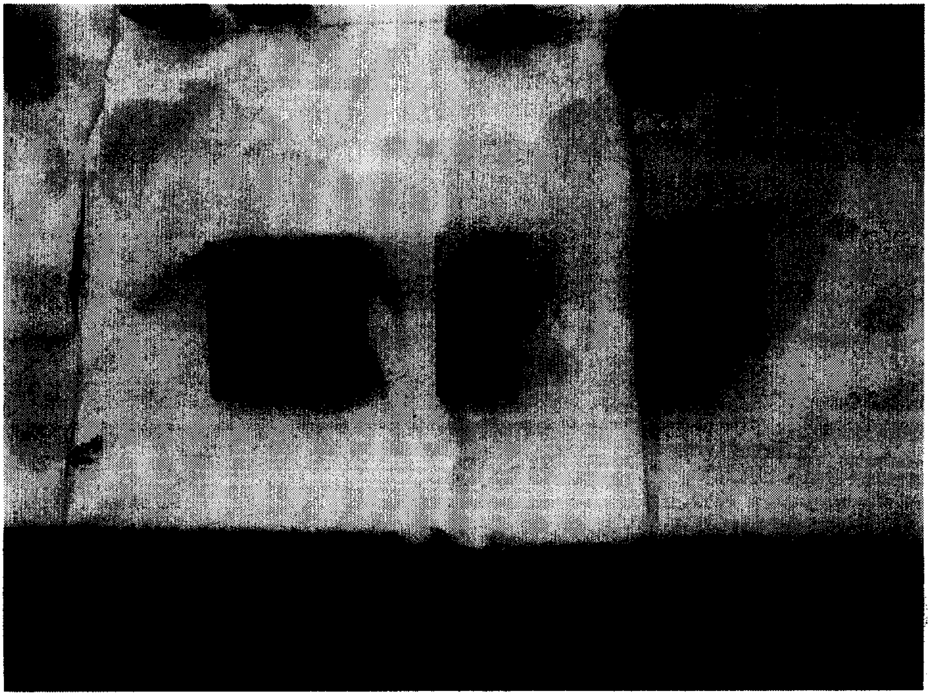

FIG. 5.
Soaked CSPG at low density showed spalling by the eighth week of curing, dry density = 13kN/M3, moisture content = 20%.

FIG. 6.
A SEM photomicrograph showing CSPG as an aggregate of PG crystals of varying size.

Discussion

The length change behavior with time for CSPG cured under moisture-controlled condition, in the presence of admixtures, was very similar for the two admixtures. There was always an initial period of expansion for the first 10-15 days followed by contraction for the lower concentrations, and slight or no expansion for the highest concentration. This behavior is also mimicked for different densities in a reverse order, there being contraction at the highest density and some or no expansion at the lowest density. There was no length change for air-cured CSPG. There is only a crude correlation between ettringite content and expansion. At fifty days, ettringite content inversely correlated with density and expansion, the specimens with highest density having least expansion and least amount of ettringite. No ettringite was detected for air-cured CSPG.

Curing under different levels of moisture can be used to understand the fate of a road base in different climates. The tests that simulate various conditions are only ideal and real world conditions are usually intermediate and will vary with time. The present study suggests that air-cured CSPG will have very little expansion or shrinkage and should be safe to use for road base construction where the risk of moisture change is small. If an appreciable amount of water is initially available to CSPG and the system subsequently stays closed, most of the expansion should occur in the first few weeks followed by little or no later expansion. A study performed on the mineralogy and microstructure of cement and PG mixtures reported that most of the

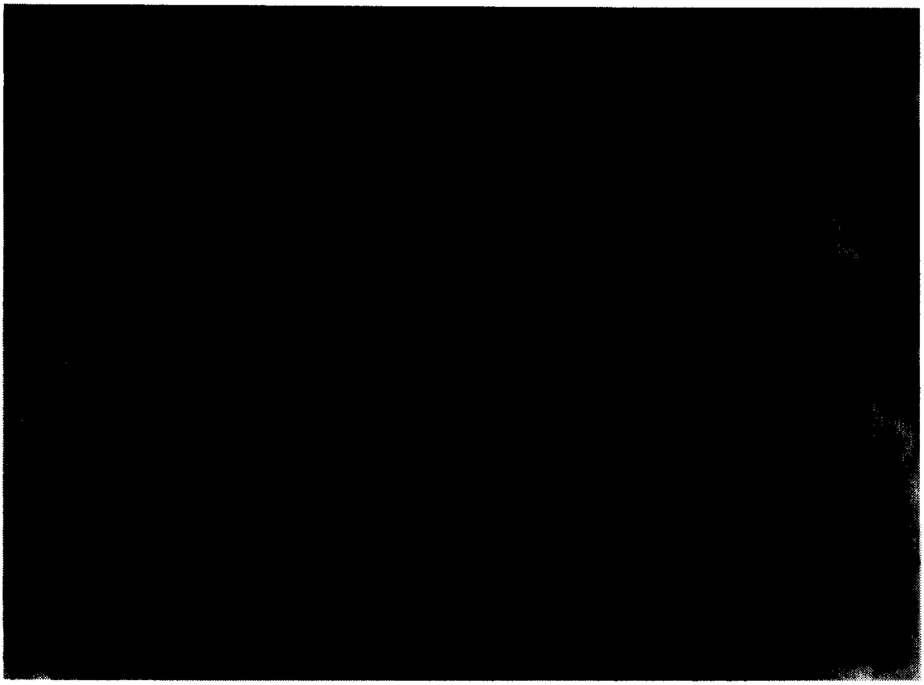

FIG. 7.
A SEM photomicrograph of a soaked CSPG specimen indicating extensive dissolution, dry density = 13kN/m3, moisture content = 20%.

ettringite in the system, under moisture-controlled condition, crystallized within the first few weeks (15). But the availability of a large amount of water, or an open system with water flowing through it, may allow a significant amount of PG to react and cause the growth of ettringite leading to deterioration (possibly failure) of the structure. These observations may explain the failure observed in the CSPG roadbases in Texas (13,14).

The durability of CSPG can be significantly improved if the dry density is increased, even if the system is open to water. However, the compactive effort needed to achieve such density on soft soils (such as those found in Louisiana) will be so great that it cannot be realized in practice (11). The addition of Daraset can also improve durability.

Ettringite growth was quite wide spread and was also found in regions where no other obvious cement phases (for example, calcium silicate hydrate) were seen (FIG. 6). Ettringite was present as a coating on the PG crystals and grew into the pores in between the grains (FIG. 8). In this instance, the ettringite must have crystallized from the reaction between PG and the cement in the immediate vicinity from solution. The growth of ettringite crystals into the existing pores is unlikely to cause much volume change. However, the crystallization of ettringite away from any calcium silicate hydrate and into PG crystals suggests that other necessary constituents of ettringite (Al, etc.) were transported to the site in solution and they diffused into the PG crystals. Volume change need not occur in this case if only solid state replacement has taken place.

Together, these observations suggest that in a sealed environment, little expansion would be expected after a few weeks. However, the exact relationship between ettringite concentration

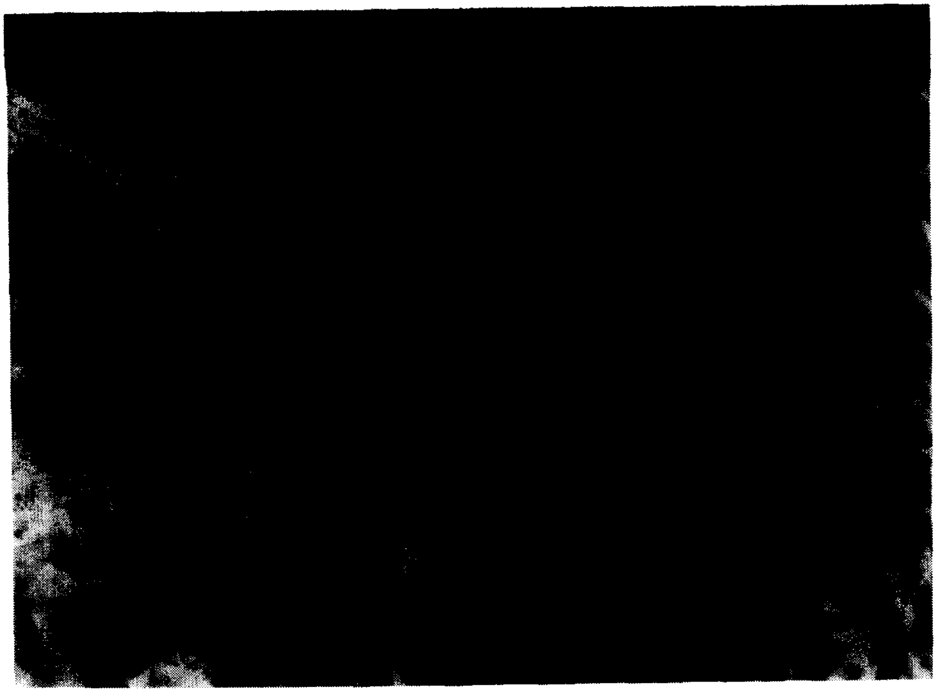

FIG. 8.

A SEM photomicrograph of a PG grain sheathed by the cementing matrix. Larger, radiating spherules of ettringite needles are also seen.

and expansion is not very clear. The present study showed that, at the same dry density, the amount of ettringite in CSPG continued to increase over time (at least up to 50 days) even though there was shrinkage after the first ten days.

The proportion of ettringite in the cement matrix (excluding the PG) observed under the SEM in soaked CSPG was as high as 50%. A Type III portland cement with 10% C_3A produces approximately 20% ettringite upon hydration (15). The Type I portland cement used in this study has a comparable C_3A content (12%). Therefore, based on the amount of cement present in the CSPG mixture, the amount of ettringite should be around 1.6%. A soaked CSPG specimen at the lowest dry density, in contrast, showed 6.7% ettringite. Thus, the amount of ettringite (Tables 1,2,3) observed in CSPG was unusually high compared to the amount of cement used. Simple calculations show that if all the dissolved sulfate from PG is converted to ettringite, substantially more ettringite should crystallize than is present in the system. Most of the dissolved sulfate from PG is probably present as sulfate ions in the percolating water.

Conclusions

The following conclusions have been derived from this study:

1. CSPG, when cured under moisture-controlled environment, irrespective of dry density, admixture content or concentration, had a short initial period of expansion. Increasing dry

density led to a period of contraction following expansion. At the same dry density, the addition of CaCl2 led to a period of no length change; the addition of Daraset led to more expansion, followed by no or little contraction. The length change, over time, of air-cured CSPG specimens was negligible. There was only a crude correlation between ettringite content and expansion.

2. For soaked specimens, ettringite growth was widespread, often away from any calcium silicate hydrate. The amount of ettringite was also unusually large, compared to the amount of cement.
3. There was appreciable dissolution of PG and visible deterioration of CSPG specimens compacted at the lowest density (13.0 kN/m3 (83 pcf)) and cured in moisture-rich environments. The dissolution of CSPG can be significantly decreased by increasing its dry density, even in a moisture-rich environment. The addtion of Daraset can also achieve the same result.

Acknowledgment

The authors would like to thank Freeport-McMoRan Inc., New Orleans, Louisiana, for their support to the Institute for Recyclable Materials, Louisiana State University, for this study.

References

1. Kalvakaalva, R. Microstructural and Phase Characteristics of Phosphogypsum and Portland Cement Mixtures, M. S. Thesis, Louisiana State University, Baton Rouge, Louisiana, (1995).
2. Taha, R., and R. K. Seals. Applications Identification of Phosphogypsum, Report I-91-3D. Institute for Recyclable Materials, Louisiana State University, Baton Rouge, May (1991).
3. H. Ölmez and E. Erdem, Cem. Concr. Res., 19, 377 (1989).
4. May, A. and J.W. Sweeney, Assessment of Environmental Impacts Associated with Phosphogypsum of Florida, US Dept. of Int., Bur. of Mines, Rep. of Investigation 8639 (1982).
5. U.S. Environmental Protection Agency, Final Regulatory Determination for Special Wastes From Mineral Processing (Mining Waste Exclusion, 40 CFR Part 261, Federal Register, Thursday, June 13, 1991, 27300-27330.
6. W.F. Chang and M. I. Mantell. Applications and Uses of Phosphogypsum Mixes. Phosphate Research Institute, University of Miami, Coral Gables, Florida, 1990, pp. 159-186.
7. D.M. Gerrity, J.B. Metcalf, and R.K. Seals, Trans. Res. Record 1440, 32 (1994).
8. Pericleous, M.I. and Metcalf, J.B., ASCE, Journal of Materials in Civil Engineering, 8, 7 (1996).
9. J.B. Metcalf and O. G. Ingles, Soil Stabilization: Principles and Practice. Butterworths, Sydney, Australia, 1972.
10. Taha, R., and R. Seals. Expansion Test Specimens - Results and Recommendations, Institute of Recyclable Materials, Louisiana State University, Baton Rouge, (1991).
11. V.S. Ramachandran, Calcium Chloride in Concrete-Science and Technology, Applied Science Publishers LTD, London, (1976).
12. S. Ong, S., J. B. Metcalf., R. K. Seals., and R. Taha, Trans. Res. Record, 1424, 20 (1993).
13. Wong, C. and Ho, M.K., The Performance of Cement-Stabilized Phosphogypsum as Base-State Highway 146, La Porte, Texas, Texas State Department of Highways and Public Transportation, DHT-11, Austin, Tx. (1988).
14. Taha, R., Utilization of By-Product Gypsum in Road Construction, Dissertation, Texas A&M University, College Station, Tx. (1989).
15. A. Roy, R. Kalvakaalva and R.K. Seals, ASCE, Journal of Materials in Civil Engineering. 8, 11 (1996).