Sulfate Attack on Stabilized and Recycled Materials in Pavements

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ABSTRACT: There have been several instances of sulfate attack on portland-cement- and lime-stabilized materials and on recycled portland-cement concrete used in pavements at US Air Force (USAF) airfields. While the chemical reactions are similar to those found in conventional sulfate attack on portland-cement concrete, the nature of the attack in a pavement setting makes conventional methods for protecting portland-cement concrete from sulfate attack ineffective for these stabilized and recycled materials. This paper will review the nature of the failures encountered on these USAF facilities. These examples show that even use of Type V sulfate-resistant cements proved inadequate to prevent attack. The paper will conclude with a discussion of our current shortfalls in knowledge and guidance in this area.

KEY WORDS: Sulfate attack, recycled concrete, cement stabilization, lime stabilization

1. INTRODUCTION

Sulfate attack is a well recognized phenomenon for portland-cement concrete, and defenses against such are well established and broadly published (e.g., American Concrete Institute 1972). The potential for sulfate attack on both lime- and cement-stabilized materials was clearly established in the laboratory in the 1950s and 1960s (Sherwood1962), but it was not until Professor Mitchell’s 1986 Terzaghi lecture (Mitchell 1986) brought attention to field problems of sulfate attack on lime-stabilized materials that the issue received much wide-spread recognition. The military, like most organizations, largely ignored the earlier work from the 1950s and 1960s that showed sulfate attack was a potential danger for stabilized materials in military pavements. However, a series of pavement failures and increased recognition of the problem in the technical literature forced the military to revamp its stabilization guidance. Warnings about sulfate attack are now included in the relevant technical manuals and educational classes. This paper briefly reviews the mechanism of sulfate attack and then examines specific cases of sulfate attack on recycled concrete and stabilized materials at U.S. Air Force facilities. Even when materials were made with Type V sulfate-resistant cements, they remained vulnerable to sulfate attack.

SULFATE ATTACK MECHANISMS

Classically, sulfate attack occurs when sulfates combine with calcium aluminate hydrate produced by hydration of the calcium aluminate phase of the portland cement to form ettringite, a potentially expansive calcium-sulfoaluminate mineral. Sulfate attack by calcium sulfate (gypsum) is described by (Taylor 1997, DePuy 1994):

$$3(CaSo_4 \cdot 2H_2O) + 4CaO \cdot Al_2O_3 \cdot 19H_2O + 17H_2O \rightarrow$$
$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$

or gypsum plus calcium aluminate hydrate plus water produces ettringite. Sodium sulfate is more soluble and hence is potentially more destructive than calcium sulfate. Magnesium sulfate is particularly destructive as the magnesium ion can also participate in reactions with the cement paste.

The volume of ettringite is over 200 percent that of the original constituents (disregarding the water) which results in massive swelling and cracking when sufficient ettringite forms by sulfation of alumina. Ettringite forms in either of two ways: (a) primary ettringite generally formed by the sulfate ion in solution acting on chemically active alumina to produce topochemical ettringite, in situ and (b) secondary ettringite formed when primary ettringite is dissolved and redeposited from solution in cracks and voids. Ettringite is only expansive when it is formed by chemical reaction; once formed it is no longer expansive. The formation of secondary ettringite is not expansive since there is no chemical reaction, only precipitation from solution, and its formation plays no part in the damage caused by sulfate attack. Similarly, primary ettringite that forms in materials that are plastic or easily deformed does not cause problems. In fact, gypsum (calcium sulfate) is usually interground with portland cement clinker to prevent premature stiffening, and such ettringite formed in the early life of the concrete is not detrimental. Once the concrete is hardened, however, formation of primary ettringite may be highly destructive.

Thaumasite ($Ca_3[Si(OH)_6 \cdot 12H_20]SO_4)(CO_3)$) is a chemical analog of ettringite with carbonate and silica substitution for alumina. The thaumasite crystal is similar to ettringite, and generally it requires X-ray diffraction to differentiate the two. Thaumasite seems to require ettringite formation (perhaps as a nucleating agent or by transformation of one to the other by substitution) and temperatures of 5 to 10^{o}C (40 - 50^{o}F) are favorable for its formation (Taylor 1997, DePuy 1994, American Concrete Institute 1992).

Protection against sulfate attack in portland-cement concrete is provided by sulfate resistant cements (U.S. Types II or V) that combat the reaction by limiting the alumina content of the portland cement phases. The maximum tricalcium aluminate (C_3A) content in Type II cement is 8 percent for moderate resistance, and for Type V is 5 percent for high sulfate resistance. Some pozzolans, slags, and silica fume have also proven effective for providing sulfate resistance for Type I (ordinary) cement and in enhancing sulfate resistance of Type II and V cements. Good mixture proportioning and construction practices that maintain low permeability in the concrete also aid sulfate resistance. Sulfate attack mitigation methods and recommended exposure limits are widely found in textbooks and professional references (e.g., American Concrete Institute 1992, DePuy 1994, Taylor 1997).

Figure 1 shows a concrete paving block manufactured with ordinary Type I portland cement that is undergoing sulfate attack. The block is dense, high strength (>1.2 MPa (>8,000 psi)), and the visible damage occurred in less than 6 months. The block in the figure is turned on its top with the bottom up where approximately 12 mm (1/2 in.) of material is gone and fragments can be popped from the remaining material with moderate pressure. The white formation visible is the ettringite, and it has formed through much of the block. The block had been laid in a bed of industrial cinders that contained the sulfates and progressive wetting and drying led to rapid attack on the bottom of the block with progressive migration upwards through the block. This attack destroys the concrete matrix resulting in a progressive almost rotting away of the concrete starting from the source of the attack. Strength alone is no protection against this chemical attack. Sulfate-resistant cements should have been used.

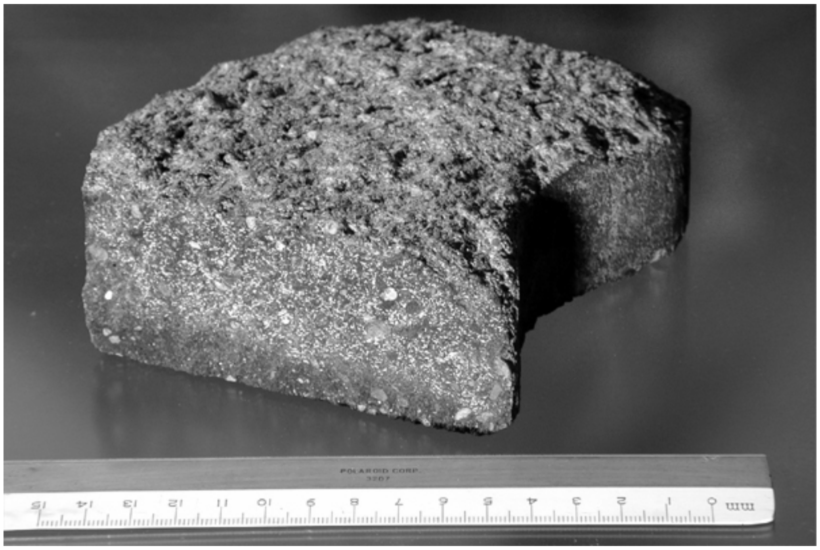

Figure 1: Concrete paving block undergoing sulfate attack.

RECYCLED CONCRETE

Since portland-cement concrete can be made resistant to sulfate attack by use of sulfate-resistant cements or addition of appropriate pozzolans and additives (fly ash, ground granulated blast-furnace slag, silica fume), one could presume that recycling sulfate-resistant concrete should pose no problems. However, recent experience at Holloman Air Force Base (AFB) has forced us to reconsider this proposition.

Holloman AFB, New Mexico is located in the Tularosa Basin. The water table is often high, sulfate exposure in local soils is very high, and the soils are typically loose fine silty sands and sandy silts. Because of the difficult site conditions, all construction on the base is placed on a minimum 0.6-m (2-ft) thick nonexpansive fill, and Type V sulfate-resistant cement is used in all concrete in contact with or near the ground. In 1995, the German Air Force, Phase 1 project (commonly known as GAF1) was built. This project consisted of a portland-cement concrete aircraft parking ramp, access taxiway, an aircraft shelter, a large maintenance hangar, and associated asphalt roads and parking lot, concrete sidewalks, and landscaped areas. Because of the grades and detailing the fill beneath this project varied from 0.6- to 2.5-m (2- to 5-ft) thick. The contractor offered and the government accepted a proposal to recycle portland-cement concrete being removed from another base location for the fill. The recycled concrete was from an approximately 40-year old airfield apron. The apron concrete showed minor age and construction defects. Its removal was necessary for structural reasons and not for any inherent defect. All records and later chemical testing indicate the concrete pavement that was recycled was made with Type V cement. It showed no signs of sulfate attack prior to its removal. The removed concrete was crushed to the well-graded gradation required for a military pavement base course and compacted to 100 percent modified density. This high-quality material was used as fill and base course throughout the GAF1 project.

Shortly after construction, heaving began, appearing initially in a few areas and then spreading in an erratic pattern. Inspections in March and July of 2000, April of 2002, January and August 2004, and February 2005 have found that the heaving is becoming progressively worse and more widespread with time. The magnitude and severity of heaving varies and several examples are shown in Figure 2. Upheaval is occurring in a variety of structures founded on the recycled concrete fill (rigid pavements, flexible pavements, foundation slabs, and sidewalks). Initial small elevation changes at the fuel trench have grown so that they now are causing cuts on tires as aircraft traverse the area. These surfaces were ground flush in 2003 but are heaving again. Doors in the maintenance hangar are sticking, and in one case where upheaval exceeded 75 mm (3 in.), the door could not be opened until the area was reconstructed. The maintenance hangar floor which is a stiff, bidirectional ribbed-mat foundation is rippled in some areas. The situation obviously is causing the owner much distress. A complete report of the site and the investigation is being published (Rollings et al 2005).

Figure 2: Examples of heaving (from left to right): heaving at door adjacent to maintenance hangar, concrete extruded from a bollard by expansion in recycled concrete base, and heaving of pavement on recycled base adjacent to fuel trench founded on subgrade.

Samples removed from the recycled concrete base found abundant ettringite and thaumasite. Sulfate attack is clearly occurring and is the probable cause of the observed heaving. No evidence was found that the heaving came from expansive soils (which can mimic many of the observed symptoms) or alkali-silica reaction (which is common on the base). Clearly, sulfate attack on this supposedly sulfate-resistant concrete is occurring.

Several factors contribute to the sulfate attack on this nominally sulfate-resistant recycled concrete. When the concrete was crushed to use as a recycled base, it became much more permeable to both water and sulfate salts in the local soil and groundwater. Consequently, the reduced alumina present in the Type V cement now had ready access to these critical contributors to sulfate attack. Dense impermeable concrete has always been considered as an important part of the protection against sulfate attack, and in a permeable crushed form, the recycled concrete is simply more vulnerable to attack than when it exists as conventional concrete. Under the paved surfaces, there is abundant moisture and sulfate available in the recycled base, and simply relying on Type V sulfate-resistant cement to combat sulfate attack is inadequate.

This failure led some to conclude that recycled concrete was a poor construction material. The proper conclusion is that recycled concrete, even when made with sulfate-resistant cements, is vulnerable to sulfate attack. Hence, recycled concrete should not be used in applications where it will be exposed to sulfates.

STABILIZATION ISSUES

Lime or portland cement may be used to stabilize soil and aggregate materials used in pavement subgrades, subbases, and bases. This stabilization may be undertaken for a variety of reasons including strengthening of the pavement section, improving marginal materials to allow their use in the pavement, modifying adverse material characteristics, or providing an all-weather construction platform. Generally, strength and durability to freezing and thawing are the primary characteristics engineers consider when dealing with pavement stabilization. However, the dangers of sulfate attack must also be weighed.

During construction of an auxiliary runway, taxiway, and ramp complex for Laughlin AFB, Texas, heaving from sulfate attack formed in the lime-stabilized subgrade. The sulfate attack damage appeared as transverse and longitudinal ridges up to 50 mm (2 in.) high, 300 to 600 mm (1 to 2 ft) wide, and 1.8 to 6.1 m (6 to 20 ft) long. During lime stabilization, the pH is raised to approximately 12. Above 9, solubility of silica and alumina rises exponentially, and this frees chemically active alumina from the soil's clay minerals. This alumina can now participate in the desirable pozzolonic reactions of conventional lime stabilization. However, if sulfate is present, it is also now free to combine with calcium from the lime and water to form ettringite. Consequently, when sulfate is present, lime-stabilized materials are vulnerable to the same chemical reactions that cause sulfate attack in conventional concrete.

Portland-cement stabilization provides the same chemical ingredients as conventional portland-cement concrete to support formation of ettringite and sulfate attack. Use of Type V sulfate-resistant cement would appear to provide the same protection to cement-stabilized materials as it does conventional concrete. This proves untrue unfortunately. As with lime stabilization, portland-cement stabilization raises the system pH thereby freeing chemically active alumina from the soil minerals to participate in the undesired formation of ettringite. This negates the usefulness of the low-alumina Type V cement. Figure 3 shows an example of sulfate attack on a taxiway's stabilized base made with Type V sulfate resistant cement.

Figure 3: Heaving of a taxiway surface caused by sulfate attack on a cement-stabilized base made with Type V sulfate-resistant cement, Holloman AFB, New Mexico.

ANALYSIS

Sulfate attack has been a recognized durability issue with conventional portland-cement concrete for over fifty years. Exposure limits and guidance for making sulfate-resistant concrete are widely published and incorporated into practice. However, when we use recycled concrete within the pavement structure, we are significantly changing exposure conditions, and guidance based on conventional concrete practice is no longer adequate. Currently, the U.S. military does not recommend using recycled concrete if there are sulfate contaminants present in the soil or groundwater that may be in contact with the recycled material. Even if this recycled concrete was manufactured with Type V cement, it may still be vulnerable to sulfate attack.

Lime and portland-cement stabilization both raise the pH of the stabilized system so that chemically active alumina is freed from clay minerals in the soil. This is the source of a needed ingredient for the formation of ettringite and ensuing sulfate attack effects. For this reason, Type V cement will not provide any protection against sulfate attack of cement-stabilized materials. Sulfate attack of stabilized materials has received more research since Professor Mitchell's Terzahi lecture in 1986 (Mitchell 1986). However, consensus on protective measures and allowable exposure limits has not been reached by the various investigators. Table 1 provides a summary of various reported sulfate attack problems on stabilized materials. Significant sulfate attack has been reported at relatively low sulfate contents and low percents of fines. Some work on countermeasures for sulfate attack on lime-stabilized materials has been conducted but results appear mixed to date. Consequently, the U.S. military currently discourages lime or cement stabilization if sulfates are present.

Table 1: Comparison of sulfate attack on stabilized materials as reported by different investigators

Project	Reference	Stabilizer	Swelling	Sulfate Content PPM	Clay-Size Fraction, %	Clay Minerals
Las Vegas Streets	Hunter 1989	Lime	Moderate to Severe	10,000	10 - 55	Halloysite with some smectite and kaolinite
			Minor	20,500	<10	
Joe Pool Lake Parks	Perrin 1992	Lime				Smectite and kaolinitic-montmorillonitic clays
Loyd Park			Severe	2,000 – 9,000	3 - 18	
Cedar Hill Park			Severe	21,200	high	
Laughlin AFB Runway	Perrin 1992	Lime	Moderate	14,000 - 25,000	34 – 63	Smectite
WES Lab Study	McCallister and Tidwell 1997	Lime	Low to Moderate	500 – 5,000		Smectite
			Moderate to Serious	5,000 – 12,000		
			Very Serious	> 12,000		
Lab Study	Mitchell and Dermatas 1992	Lime	Slight to Severe	0.3 – 6.2%	30	Kaolinite
			None to Moderate	0.3 – 6.2%	30	Montmorillonite
Georgia Road	Rollings et al 1999	Portland Cement	Moderate		6 – 13	Halloysite with some smectite and kaolinite
Holloman AFB Taxiway		Portland Cement	Severe	High	33 - 56	Kaolinite and Chlorite

Notes: Information as reported by authors. Consistent definitions and sulfate measurement techniques not used between different investigators. PPM is parts per million. Clay-sized fraction is percent < 0.002 mm. Holloman AFB reporting percent passing the No. 200 sieve.

More research is needed to provide improved guidance on at what threshold sulfate attack becomes a threat to stabilized materials, what characteristics of the soil are involved (clay mineralogy and clay content), and what countermeasures are effective in mitigating this sulfate attack of stabilized materials.

Sulfates are most often associated with arid and semiarid regions, and the authors have commonly dealt with sulfate contaminant problems in the America Southwest and the Middle

East. However, sulfates are not limited to such areas. The authors have also encountered sulfate attack problems with a clay in Mississippi, leachate from a coal storage yard in Virginia, industrial cinders in Ohio, and well water used for compaction in coastal Georgia. In New Orleans where aggregates are scarce, an industrial waste was crushed and cement-stabilized for use as a base course in a flexible pavement. The waste was calcium sulfate hemihydrate, and sulfate-attack heaving soon appeared. It is important to recognize that sulfate exposure is not limited to arid regions alone.

CONCLUSIONS

Guidance and appropriate countermeasures are well established for dealing with sulfate attack of conventional portland-cement concrete. However, when we use even nominally sulfate-resistant concrete recycled as fill, base, and subbase in a pavement structure, we are radically changing the exposure conditions. In this form, the recycled concrete may be vulnerable to sulfate attack. No guidance on allowable exposure levels for recycled concrete is available, and the existing guidance based on conventional concrete is not appropriate. Lime- and cement-stabilized materials are also vulnerable to sulfate attack. Because of the high pH environment that exists in stabilized materials, alumina can be freed from the clay minerals in the stabilized soils and aggregates. This is a significantly different chemical situation from that encountered with conventional portland-cement concrete. Consequently, existing guidance from conventional concrete technology on allowable sulfate exposure and on use of low-alumina sulfate-resistant cements to mitigate sulfate attack is ineffective. More research is needed to identify under what conditions recycled concrete and stabilized materials are vulnerable to sulfate attack and what countermeasures are effective in combating this sulfate attack. While sulfates are most commonly associated with arid and semiarid regions, there are a number of potential sources of sulfate contamination in more temperate and humid climates.

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REFERENCES

American Concrete Institute. Guide to Durable Concrete, Committee Report 201.2R-92, 1992.

DePuy, G. 1994. “Chemical resistance of concrete,” *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, P. Klieger and J. Lamond, editors, STP 169C, American Society for Testing and Materials.

Hunter, D. 1989. “The Geochemistry of Lime-Induced Heave in Sulfate Bearing Clay Soils” PhD Dissertation, University of Nevada, Reno, Nevada.

McCallister, L. and L. Tidwell. 1997. “Double lime treatment to minimize sulfate-lime induced heave in expansive clays,” Internal Report, USAE Waterways Experiment Station, Vicksburg, Mississippi.

Mitchell, J. 1986. “Practical problems from surprising soil behavior,” ASCE *Journal of Geotechnical Engineering*, Vol. 112, No. 3.

Mitchell, J. and D. Dermatas. 1992. “Clay soil heave caused by lime-sulfate reactions,” *Innovations and Uses for Lime*, STP 1135, D. C. Hoffman and D. D. Stanley, editors, American Society for Testing and Materials, Philadelphia, Pennsylvania.

Perrin, L. 1992. “Expansion of lime-treated clays containing sulfates,” *Proceedings*, 7th International Conference on Expansive Soils, Vol. 1, Dallas, Texas.

Rollings, R., J. Burkes and M. Rollings. 1999. “Sulfate attack of a cement-stabilized sand,” ASCE *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 125, No. 5.

Rollings, R., M. Rollings, T. Poole, G. Wong, and G. Gutierrez. 2005. “Investigation of heaving at Holloman AFB, NM,” accepted for publication by ASCE *Journal of Performance of Constructed Facilities*.

Sherwood P. T. 1962. “Effect of sulfates on cement and lime-stabilized soils, Highway Research Board Bulletin 353, National Research Council, Washington D.C., 1962.

Taylor, H. 1997. *Cement Chemistry*, 2nd edition, Thomas Telford Publishing, 1997