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Guest Editorial

Thaumasite formation and other forms of sulfate attack

This volume contains papers emphasizing thaumasite formation, while considering other forms of sulfate attack. The purpose of this introduction is to briefly summarize various forms of sulfate attack to provide a context for the papers which appear within.

The classic form of sulfate attack, associated with the ingress of sulfate ions, has been understood for nearly a century as a series of phenomena affecting concrete durability. However, sulfate attack may manifest in a variety of ways and the origins of the sulfates may be both external and internal. The list of forms of sulfate attack increases in concert with advances of our understanding of the relevant phenomena. The following forms of sulfate attack have been recognized in the literature:

- The classic form of sulfate attack associated with ettringite and/or gypsum formation.
- Physical sulfate attack associated with the crystallization of sulfate-containing salts at or near an evaporative surface.
- Delayed ettringite formation.
- Sulfate attack associated with the formation of AFm phases.
- Thaumasite formation.

In classic sulfate attack, adjacent solutions containing dissolved sulfates intrude concrete pore structures. These sulfates move through concrete porosity by diffusive or advective flow. In doing so they may then react with sources of calcium to form gypsum and with sources of alumina to eventually form ettringite. Depending on the source of alumina, ettringite formation may occur directly or its formation may be preceded by that of monosulfate. The latter is more likely in concrete containing mineral admixtures in that they supply supplementary sources of alumina. In spite of an increased potential for ettringite formation, blended cements are generally regarded as more resistant to sulfate attack because of their greater impermeabilities. Al-Amoudi discusses this when comparing the sulfate resistance of plain and blended cements.

Although the mechanistic path of classic sulfate attack is reasonably well understood with respect to the formation of those compounds which cause damage, related forms of damage are frequently not considered. A typical measure of sulfate attack in mortar laboratory samples is the extent of expansion. However, sulfate attack in field concrete may cause significant microstructural damage leading to the formation of networks of cracks, in the absence of macroscopic expansion. Other forms of microstructural damage include $Ca(OH)_2$ dissolution, as Ca is required for the formation of ettringite and gypsum. Unless the factors resulting in microstructural alteration are considered, it will be difficult to predict the long-term performance of cementitious systems. Several approaches have been used. The behavior observed in short-term tests has been used as a predictive tool. Other approaches have involved investigation of the properties of natural analogs or the analyses of ancient materials. The most fundamental approach is to develop a model to describe the relevant behavior. Marchand et al. describe a model permitting the prediction of durabilities of concretes exposed to dilute sulfate solutions.

Not all the sulfate entering the concrete pore structure reacts internally. Depending on the permeability characteristics of the concrete and the site location, some proportion of the sulfate may migrate to evaporative fronts. Physical sulfate attack of concrete may occur when sulfate salts accumulate at, or near, exposed surfaces of concrete. Physical sulfate attack can be regarded a specific type of salt damage. A common form of physical sulfate attack occurs when sodium sulfate crystallizes in the concrete pore structure. In this regard, physical sulfate attack shares features in common with frost damage. It has been observed that the crystallization of NaCl in concrete resulted in the formation of crystalline salt columns reminiscent of ice needles, and that this resulted in physical attack of the concrete. Salt damage is not unique to Portland cement concrete; it has also been reported to occur in bituminous concrete. Indeed, salt damage is generic to porous media through which electrolytes are transported.

The typical consequence of physical sulfate attack of concrete is surface erosion. In its early stages, it is manifested primarily by the appearance of white crystallites (efflorescence) on a concrete surface. Two factors

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contribute to the damage. The first is the direct crystallization of a salt, most commonly sodium sulfate. It is not unusual, however, for gypsum to crystallize or mixed crystals containing sodium, calcium sulfate, chloride, and carbonate to form. Less frequently magnesium sulfate crystallizes. The extent of damage will depend on a variety of factors. These include the amount and composition of sulfate-containing solution transported through the pore structure, the location of the evaporative front, the frequency of heating and cooling cycles. The composition of the sulfate salt formed is also important; sodium sulfates may interconvert between the 10 hydrate and the anhydrous salt. Thernardite has been reported to be capable of producing pore pressures of 400–5000 psi while mirabilite produces pore pressures of 1000–1200 psi. Although the equilibrium temperature for interconversion is approximately 30 °C, this temperature is reduced in the presence of chloride ion.

The proportion of the aluminate phase in Portland cement is of direct concern when designing a concrete to be sulfate resistant. Increased sulfate resistance at a constant water-to-cement ratio is associated with a reduction in the C_3A content of a cement. Indeed, ASTM Type V cement was developed for the sole purpose of providing a means to exhibit some compositional control of sulfate attack. However, even so-called zero C_3A cements are not immune from sulfate attack. As a further indication that compositional control itself may be inadequate to eliminate sulfate attack, Clark and Brown provide data indicating that the ferrite phase, in particular, may react with sulfate solutions to form gypsum, ettringite, and monosulfate. As a number of papers in this volume indicate, control of permeability is of greater importance than compositional control.

The sulfate ions participating in sulfate attack may be present in the concrete at the time of mixing or they may have entered the concrete from an external source. It is well recognized that concrete can be damaged in the event that ettringite formation continues after substantial hardening has occurred. For this reason, sulfate is carefully proportioned in cement manufacture. While the mechanistic details associated with delayed ettringite formation (DEF) are still being established, this form of sulfate attack is primarily associated with concretes containing high-early strength cements cured at elevated temperatures. This combination of materials selection and curing regime resulted in extensive damage to railroad sleepers (ties) in Europe and North America. The CSH formed in curing at elevated temperature competes for the sulfate that would normally react to form ettringite. In delayed ettringite formation, damage occurs in the absence of the ingress of external sulfate and ettringite forms in hardened concrete as this bound sulfate is slowly released.

Expansion caused by monosulfate phase formation was first reported by Chatterji in 1968. While it has been demonstrated that the stability of ettringite is decreased by alkali, the U phase can readily form in solutions equivalent to pore solutions in concrete. The U phase is a sodium substituted AFm that was discovered by Dosch and zur Strassen in 1966. U phase formation may play a role in sulfate attack in that it has been reported to cause expansion.

An appropriate representation of the structure of ettringite is as: $[Ca_3Al(OH)_6 \cdot 12H_2O^{3+}]_2(SO_4^{2-})_3 \cdot 2H_2O$. In the unit cell, $Ca_3Al(OH)_6$ units form four columns per cell. These are highly hydrated. There are four interstices between the columns per unit cell. Three of these are occupied by sulfate anions and the fourth is occupied by two molecules of water. The nature of this structure permits a broad range of substitutions: divalent cations can be substituted for calcium; trivalent cations, such as transition metal ions, can substitute for aluminum; tetravalent ions, such as Si^{4+}, can also substitute for aluminum. Such a silica-based compound is thaumasite, $2CaO \cdot SiO_2 \cdot 2CaSO_4 \cdot 2CaCO_3 \cdot 30H_2O$. Thaumasite was first identified as occurring in deteriorating concrete in 1965. Ettringite and thaumasite are frequently found together in deteriorating concrete. It has been debated whether they are present as intimate mixtures or whether they exhibit solution behavior when formed under these conditions. Barnett et al. follow the phase evolution of thaumasite/ettringite and characterize their solid solution behavior. Sahu et al. assess the Raman spectra of thaumasite and ettringite as a diagnostic tool.

Thaumasite formation can occur in the absence of external sulfate as carbonation decomposes the C–S–H binder. External sulfate can also contribute to thaumasite formation. Similarly, if a source of $CaCO_3$ is present within the concrete, thaumasite formation may occur. Thus, thaumasite formation may occur as a consequence of sulfate ingress, of carbonation, or both. Hartshorn et al. discuss thaumasite formation in mortars exposed to magnesium sulfate while Brown and Hooton discuss thaumasite and ettringite formation in concretes exposed to sulfate solutions for over 20 years.

Interest in extending cements using limestone flour has increased. Therefore, it is important to develop a deeper understanding of the conditions under which thaumasite formation may occur and cause damage to concrete containing finely ground calcium carbonate. Tsivilis et al. describe the extent of use of Portland-limestone cements.

While originally thought to occur only in concretes exposed to cool temperatures, thaumasite formation has been observed in concrete placed in temperate climates. Sahu et al. demonstrate that thaumasite formation can occur in concrete placed in a warm climate. They also demonstrate that thaumasite may form in the products of coal combustion. As with ASR, for example, some common forms of deterioration have been slow to have been recognized. Indicating a growing recognition, Crammond provides an extensive review of the occurrence of thaumasite formation in construction.

P.W. Brown
Penn State University
136 MRL, University Park
PA 16802, USA
E-mail address: etx@psu.edu