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Note

“Sulfate attack,” or is it?

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Abstract

Studies of, and articles on, sulfate attack have frequently assumed that this destructive mechanism simply involves the production of ettringite or gypsum. The complexity of “sulfate attack,” and of mechanisms masquerading as sulfate attack, are detailed.

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“Sulfate attack” on concrete has been reported to be a cause of damage to concrete for over a century. However, the term “sulfate attack” has been used in the literature to describe at least six types of reaction, only one or two of which are classical sulfate-attack mechanisms that specifically involve the sulfate ion acting chemically.

The chemical equation for ettringite formation in fresh cement paste, mortar, or concrete, shown in Eq. (1), is often used to define textbook sulfate attack:

$$\begin{aligned} &\underset{\text{gypsum}}{3(CaSO_4 \cdot 2H_2O)} + \underset{\text{tricalcium aluminate}}{3CaO \cdot Al_2O_3} + \\ &\underset{\text{water}}{26H_2O} \rightarrow \underset{\text{ettringite}}{3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O} \qquad (1) \end{aligned}$$

This reaction is often described as involving expansion, but as pointed out (e.g., by Hansen and Offutt [1]), there is a contraction in volume when all the reactants originate within the system. The numbers in the first line below the chemical formulas are the volumes of the compounds. The number in parentheses is the volume to be added to those on the right-hand side to equal the volumes on the left-hand side, as shown in Eq. (2):

$$\begin{aligned} &\underset{88.8}{3CaO \cdot Al_2O_3} + \underset{222.3}{3CaSO_4 \cdot 2H_2O} + \underset{468.5}{26H_2O} = \\ &\underset{725.1}{3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O} \qquad (2) \end{aligned}$$

Thus expansion need not be a necessary result of the Equation (1) reaction.

For hardened concrete there can be several sources of calcium and sulfate, and the aluminate may be supplied by tricalcium aluminate hydrates or by monosulfoaluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$), or by the chemically active alumina in Class C fly ash. Therefore sulfate attack that leads to expansive ettringite formation is best described by the ionic equation, Eq. (3):

$$\begin{aligned} &6Ca^{+2} + 3SO_4^{-2} + Al_2O_6^{-6} + \\ &32H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \qquad (3) \end{aligned}$$

This generic equation should not be taken to imply that the reactants are necessarily species dissolved in water, or as noted above, that all such reactants cause expansion. For example, the aluminate phase may be a solid, requiring a topochemical reaction.

Several investigators report that Eq. (3) represents the only sulfate-attack mechanism. However, others state that the formation of gypsum is also an expansive sulfate-attack mechanism. The two usual reactions that produce gypsum in hardened concrete involve sodium or magnesium sulfate solution are shown in Eq. (4) and Eq. (5):

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH \qquad (4)$$

$$\begin{aligned} &Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow \\ &CaSO_4 \cdot 2H_2O + Mg(OH)_2 \qquad (5) \end{aligned}$$

Numerous scientists, however, report that gypsum production does not cause concrete deterioration. It is unlikely,

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for example, that dissolution of gypsum in soil and subsequent reprecipitation in contacting concrete is expansive. That is [Eq. (6)]:

$$Ca^{++} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{6}$$

is probably an innocuous reaction. Further, the production of $Mg(OH)_2$ (brucite) by Eq. (5), when caused by magnesium sulfate solutions entering hardened concrete, occurs at the concrete surface and may "case harden" the structure and actually retard sulfate-attack damage.

Unfortunately, sodium sulfate and magnesium sulfate can each lead to at least four distress mechanisms. For sodium sulfate, Eq. (4) followed by Eq. (3) represents two "sulfate-attack" mechanisms. However, two other distress mechanisms also apply, as represented by Eq. (7) and Eq. (8):

$$2Na^{+} + SO_4^{-2}(\text{aqueous}) \rightarrow Na_2SO_4(\text{solid}) \tag{7}$$

This mechanism is sometimes called "salt crystallization" and usually involves repeated dissolution of the solid sodium sulfate and recrystallization in concrete pores. Some literature indicates that other salts, such as sodium chloride, nitrate, or sulfate, when dissolved from soil and subsequently absorbed into the surface region of concrete, crystallize as the water evaporates, leading to large crystallization or osmotic pressures. Precipitation from supersaturated solution may be required for deleterious action.

Slight variations in temperature and relative humidity cause the following reversible reaction, as seen in Eq. (8):

$$\underset{\text{thenardite}}{Na_2SO_4} + 10H_2O \leftrightarrow \underset{\text{mirabilite}}{Na_2SO_4 \cdot 10H_2O} \tag{8}$$

The left-to-right reaction involves a large expansion. This reaction is the basis for testing aggregates by ASTM C 88 (Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate), in which porous particles are immersed in sodium or magnesium sulfate solution, then dried in an oven so that the hydrated salt precipitates and dehydrates, and is subsequently rehydrated when the material is returned to the sulfate solution. The resultant destructive force, intended to simulate the expansion of water on freezing, is caused by the change from the anhydrous to hydrated state [Eq. (8)]. Obviously this is not a classical sulfate attack mechanism since neither gypsum nor ettringite is formed, and indeed is not "salt crystallization," although it is often called so.

For magnesium sulfate, the reaction shown in Eq. (5) followed by the reactions in Eq. (1) or Eq. (2) are sulfate-attack mechanisms. Corresponding to sodium sulfate, magnesium sulfate can also cause damage, as shown in Eq. (9) and Eq. (10):

$$Mg^{+2} + SO_4^{-2} \rightarrow MgSO_4 \text{ (or hydrates of it),} \tag{9}$$

and hydration expansion by

$$MgSO_4 + \overset{H_2O}{\leftrightarrow} \underset{\text{kieserite}}{MgSO_4 \cdot H_2O} + \overset{5H_2O}{\leftrightarrow} \underset{\text{hexahydrate}}{MgSO_4 \cdot 6H_2O} + \overset{H_2O}{\leftrightarrow} \underset{\text{epsomite}}{MgSO_4 \cdot 7H_2O} \tag{10}$$

However, dehydration of epsomite occurs only at temperatures above 70°C, so the reverse reaction is unlikely under most conditions.

Magnesium sulfate can also cause distress to concrete by decreasing the concentration of hydroxide ion in accordance with Eq. (5). To reestablish equilibrium, the calcium silicate hydrate ("CSH") phase may decompose, causing loss of strength. Magnesium silicates can also be produced, releasing hydroxide ion.

It is obvious that if sodium sulfate and magnesium sulfate solutions contact concrete, distress not related to sulfate attack and not related to type of cement, and possibly not to water-cement ratio, may occur. All of this was dramatically disclosed by recent findings of the Portland Cement Association and its Construction Technology Laboratories affiliate [2] during their study of their Sacramento Test Plot samples. Prisms placed in sodium and magnesium sulfate exposures were found to have undergone severe distress after many years but, during removal of the below-ground portions that were directly in contact with the sulfates, it was found that they appeared undistressed. Companion prisms completely immersed in 10% solutions of the salts have not evidenced distress. A logical (but perhaps premature) conclusion is that sulfate attack caused no distress, but such processes as thenardite/mirabilite conversion and salt crystallization caused all of it.

To complicate the above analysis, many soils contain sulfuric acid due to oxidation of iron sulfides (pyrite or marcasite). Acid attack can also occur and the distress caused by the acid may masquerade as sulfate attack [3], especially since gypsum is the major product of the reaction.

To predict time to failure of concrete structures exposed to sulfate it is obvious that one must know what cations (e.g., sodium, magnesium, hydrogen, or calcium) accompany the sulfate. Just as obviously, one should not predict distress due to gypsum in soil by use of experiments employing, for example, sodium sulfate, nor should prediction of below-ground deterioration be based on studies where evaporation may be the driving mechanism.

Additionally, the location of the reactants and products is important (e.g., secondary ettringite in voids is no indication of distress), and factors such as carbonation and exposure to moisture can significantly affect, for example, ettringite or magnesium hydroxide formation.

We need more research and analysis [4] to:

1. Restudy the world's sulfate-attack literature.
2. Determine the effect of each of the sulfate compounds on concrete as a function of cement type and content and water-cement ratio.

3. Determine distinguishing features of each of these types of reaction to prevent misdiagnosis and improper or unnecessary repair.

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