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Discussion

Discussion of the paper "Sulfate attack," or is it? by W.G. Hime and B. Mather[☆]

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We read with interest the note by W.G. Hime and B. Mather [1] regarding their concerns about what is sulfate attack. The essence of their concise overview can be found in most standard textbooks [2–5], where it is clear that the term "sulfate attack" is used to mean deterioration of concrete matrix by sulfate-bearing aqueous solutions. It is often useful to go back to earlier literature such as Biczok [6] and the "Thorvaldson Symposium" [7], which clearly emphasizes the multifaceted nature of the sulfate problem. Expansion that is sometimes associated with ettringite formation may be the best-publicized manifestation of sulfate attack, but it is often overshadowed by other simultaneous sulfate-related reactions, such as decalcification of C-S-H in the presence of magnesium sulfate. DePuy [8] in a recent review also emphasizes the overreaching use of the term "sulfate attack" and includes reactions other than ettringite and gypsum formation.

It is also worth noting that in early field studies [7], including the Sacramento Field Trials referred to by Hime and Mather, microstructural or chemical studies (e.g., identification of reaction phases) were seldom undertaken (and have not been reported for the Sacramento Test Plots). Therefore, we do not see a solid technical basis for the claim that "classical" sulfate attack involves only gypsum and ettringite formation, as Mather himself pointed out in an earlier paper [9]. Their formation may be a "classic example" in that it is a frequently observed phenomenon, but as Hime and Mather noted themselves, how any of the reaction processes cited will affect deterioration of a particular concrete depends on a variety of factors, including rates of mass transport and the mode of initiation of adverse chemical reactions. An example of sulfate reaction completely omitted by Hime and Mather is formation of thaumasite, a process apparently unrelated to the C_3A content.

Verbeck [10], in his initial analysis of the Sacramento data, points out the critical role of water/cement ratio in preventing sulfate attack. The water/cement ratio, together with the degree of hydration (regulated by curing conditions), controls the permeability and other transport properties. The important role of transport properties in controlling not only the deterioration of concrete exposed to sulfate-bearing waters, but also all other forms of chemical attack, is now generally recognized.

Ettringite, as correctly stated, may or may not cause expansion; this fact has been well known for decades and has been recently discussed [11–13]. As a matter of fact, ettringite "expansiveness" is not the real issue as ettringite per se is nonexpansive. The more important issue is the physicochemical and environmental *conditions* under which ettringite forms: temperature and presence of moisture; changes in temperature and humidity; composition and concentration of chemical species present in the system and their relevant solubilities; total pore space and its distribution; etc.

There is no credible evidence supporting the notion that topochemical formation of ettringite is the basis of expansion. All topochemical reactions require matching of atomic distances between the reactant and product but, as Brown and Taylor [14] point out, the crystal structures of C_3A and ettringite are totally unrelated. Apart from this, recent microanalytical investigations show that in the case of external sulfate attack the ettringite is not preferentially formed in space previously occupied by C_3A, or even at the surfaces of any unreacted C_3A, but in intimate mixture with C-S-H. Furthermore, the formation of ettringite from C_3A and gypsum is preceded by intermediate reactions [15]. Note also that expansion due to so-called delayed ettringite formation (DEF), which occurs without direct involvement of C_3A.

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Topochemical formation of ettringite has been questioned already by Hansen [16].

The formation of brucite at external surfaces is frequently observed and when it does, it can provide beneficial protection referred to as "case hardening." However, it cannot be argued that brucite does not form elsewhere, and indeed both brucite and magnesium silicate have been observed beneath the surface in recent detailed studies of high porosity, high-permeability concrete [17,18].

Another category of sulfate attack (!) is represented by the deterioration of concrete by sulfuric acid or ammonium sulfate solutions. In such cases, sulfate attack is supplemented by acid attack and the damage attributable to the acid component may be significant. Similar combination of deleterious reactions may take place when soils contain iron sulfides that may oxidize to sulfates.

The attempts to draw a distinction between "physical" and "chemical" processes does not serve a useful purpose and will only serve to further confuse engineers. The so-called "salt crystallization," in this case referring to repeated recrystallization of mirabilite to thenardite and vice versa, is neither "salt crystallization" nor "physical sulfate attack." Phase changes such as conversion from one hydrate to another, or crystallization from solution, represent a *chemical* change. The physical manifestations of the process should not be divorced from the underlying chemical changes. All are physicochemical processes.

We agree that in some cases more analytical work and research is needed to clarify details of the physicochemical processes underlying deterioration of concrete and the interactions between bulk transport and chemical change. But we would argue that the essential knowledge is already available. A more critical interpretation (and subsequent application) of existing knowledge would almost certainly avoid most problems of sulfate attack. Regrettably, Hime and Mather have not provided that interpretation.

References

[1] W.G. Hime, B. Mather, "Sulfate attack," or is it?, Cem Concr Res 29 (1999) 789–791.

[2] S. Mindess, J.F. Young, Concrete, Prentice Hall, 1981.

[3] P.K. Mehta, P.J.M. Monteiro, Concrete: Microstructure, Properties, and Materials, 2d ed., McGraw-Hill, New York, 1993.

[4] H.F.W. Taylor, Cement Chemistry, 2d ed., Thomas Telford, London, 1997.

[5] M. Eglington, Resistance of concrete to destructive agencies, in: P. Hewlett (Ed.), Lea's The Chemistry of Cement and Concrete, 4th ed., Arnold, London, 1998, pp. 299–342.

[6] I. Biczok, Concrete Corrosion, Concrete Protection, Akademiai Kiado, Budapest, 1972.

[7] E.G. Swenson (Ed.), Performance of Concrete, University of Toronto Press, Toronto, 1968.

[8] G.W. DePuy, Chemical resistance of concrete, in: P. Klieger, J.F. Lamond (Eds.), Tests and Properties of Concrete, ASTM STP 169C, 1994, 263–281.

[9] B. Mather, Field and laboratory studies of the sulfate resistance of concrete, in: E.G. Swenson (Ed.), Performance of Concrete, University of Toronto Press, Toronto, 1968, p. 66.

[10] G.J. Verbeck, Field and laboratory studies of the sulfate resistance of concrete, in: E.G. Swenson (Ed.), Performance of Concrete, University of Toronto Press, Toronto, 1968, p. 113.

[11] I. Odler, I. Jawed, Expansive reactions in concrete, in: J. Skalny and S. Mindess (Eds.), Materials Science of Concrete, Volume II, The American Ceramic Society, Westerville, OH, 1991, pp. 221–247.

[12] H.F.W. Taylor, Sulfate reactions—Microstructural and chemical aspects, in: E.M. Gartner, H. Uchikawa (Eds.), Cement Technology, Ceramic Transactions 40, The American Ceramic Society, Westerville, OH, 1994, pp. 61–78.

[13] Ettringite in cement paste and concrete, in: J.-P. Bournazel, Y. Malier (Eds.), Concrete: From Materials to Structure, Conference in honor of Micheline Moranville, Arles, September 1996, RILEM, 1998, pp. 55–76.

[14] P.W. Brown, H.F.W. Taylor, The role of ettringite in external sulfate attack, in: J. Marchand, J. Skalny (Eds.), Mechanisms of Sulfate Attack, Special Volume of Materials Science of Concrete, The American Ceramic Society, Westerville, OH, 1999, pp. 73–97.

[15] I. Jawed, J. Skalny, J.F. Young, in: P. Barnes (Ed.), Structure and Performance of Concrete, Applied Science, 1983, pp. 273–275.

[16] W.C. Hansen, The chemistry of sulphate-resisting Portland cements, in: P. Hewlett (Ed.), Lea's The Chemistry of Cement and Concrete, 4th ed., Arnold, London, 1998, pp. 18–54.

[17] S. Diamond, R.J. Lee, Microstructural alterations associated with sulfate attack in permeable concretes, in: J.-P. Bournazel, Y. Malier (Eds.), Mechanisms of Sulfate Attack, Special Volume of Materials Science of Concrete, The American Ceramic Society, Westerville, OH, 1999, pp. 123–173.

[18] J. Skalny, S. Diamond, R.J. Lee, Sulfate attack, interfaces and concrete deterioration, in: A. Katz, A. Bentur, M. Alexander, G. Arliguie (Eds.), The Interfacial Transition Zone in Cementitious Composites, Proceedings of the International RILEM Conference, E&FN SPON, London and New York, 1998, pp. 141–151.