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Discussion of "The Process of Sulfate Attack on Cement Mortars" by Shen Yang, Xu Zhongzi, and Tang Mingshu*

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The experiments[1] described by Yang et al. are very ingenious and provide a convincing demonstration of the importance of the role played by the interfacial zone between cement paste and aggregate in solution-based chemical attack on mortars and concretes. The data developed from these experiments are a worthwhile contribution to improved understanding of the process of chemical attack, an understanding that Professor Cohen and I emphasized in 1991 [2] as being in need of improvement as it relates to sulfate attack.

There are some aspects of the paper that I wish to discuss for purposes of clarification. I take them up in the order they are found in the paper.

(1) Page 1, column 1, lines 6–8: The authors cite Taylor [1] as their authority for their statement that expansion is generally attributed to the formation of ettringite and gypsum; there are other references that also say this. However, I have seen no evidence that the formation of gypsum during sulfate attack on cement paste causes expansion. I believe the gypsum forms primarily, if not exclusively, by reaction of sulfate ion with calcium ion and precipitation of gypsum from a solution that by evaporation, becomes supersaturated. If this is the process, no expansion would be expected to result. You cannot break a bottle full of a saturated solution by removing the cork and letting the water evaporate.

(2) Page 1, column 1, lines 4–5 from end: The authors give no reference for their statement that the sulfate solution that penetrates the mortar reacts with "crystals such as calcium hydroxide and calcium sulfoaluminate." I doubt that this is the principal thing that happens. I believe the sulfate reaction that produces gypsum is through solution, not sulfation of solid $Ca\ (OH)_2$. "Calcium sulfoaluminate," if ettringite, is already fully sulfated; if monosulfate, then it could be sulfated in situ and expand, but if monosulfate, it presumably is occupying space in the paste that was occupied by earlier formed ettringite which was altered to monosulfate as the sulfate level in solution fell. Hence, unless the space subsequently became occupied by other substances, the monosulfate could topochemically resulfate to ettringite without causing expansion of the system.

The primary and only well understood expansive reaction that is involved in sulfate attack is the in situ, topochemical sulfation of unsulfated or undersulfated, unhydrated or hydrated calcium aluminates or calcium aluminate monosulfates, as described by Hansen [10] and others.

(3) Page 1, column 2, line 7 from end: The authors refer to "normal quartz sand" as "inert to water and sulfates." It would have been more correct to say "relatively non-reactive to water and sulfates." Nothing is inert.

(4) Page 3, column 1, line 13 from end: The authors here refer to the reactants: "calcium hydroxide and calcium monosulfoaluminate."

(5) Page 3, column 2, "The SEM Examination": The authors report that certain needle-shaped products were "verified to be gypsum" by EDXA and XRD. They did not say that ettringite was looked for and not found. This circumstance caused me to go back and note that on page 1, in column 2, in the eleventh line from the end, the authors state that the cement used had properties "similar to that of ASTM Type 1 (sic)" but "is lower in aluminate." From the data reported in Table 1 of the paper being discussed, the cement had 4% C_3A, calculated as prescribed in ASTM C 150, which makes the cement much more similar to ASTM Type V than to ASTM Type I. This may be why no sulfate attack of the normal, ettringite-producing variety took place and why no ettringite was reported as a reaction product.

Because it appears that the only sulfates involved in these studies are Na_2SO_4 and $CaSO_4 \cdot 2H_2O$, the question arises as to whether precipitation of a hydration product of Na_2SO_4 and its dehydration and rehydration, as in the ASTM C 88 soundness test, could have been involved in the production of the observed expan-

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sion. The testing process as described seems to preclude this. However, the work of Binda and Baronio [11] might be reviewed.

(6) On page 3, column 2, the next to last line: The authors speak of gypsum as "the product of sulfate attack." The gypsum is quite probably the product of reaction with the sulfate ion in the penetrating fluid, but no evidence is given here or elsewhere to suggest that this reaction constitutes an "attack" that caused or would be expected to cause any loss of integrity to the mortar.

My conclusion is that it is a pity that so elegant and ingenious a set of experiments relating to chemical attack on mortar were conducted on the assumption that the results might illuminate our knowledge of sulfate attack when, in fact, they fail to do so because the cement chosen for use was almost completely resistant to sulfate attack. It appears that negligible amounts of ettringite were formed. I hope the authors may be able to repeat the work with a cement of the order of 10 to 15% calculated C_3A.

We did some work [12] with three cements of 5.1, 9.2, and 12.5% calculated C_3A content; $w/c = 0.5$; and cement-sand ratios of 1:20, 1:275, and 1:35. The expansions of the mortars at 16 weeks with 5 and 9% C_3A were negligible but with the 12.5% C_3A cement, the 1:35 cement to sand mortar had 4.4% length increase; the 1:275 cement to sand mortar had 1.02% increase; and the 1:20 cement to sand mortar had 0.20% increase. These results suggest that if the mortars studied by the authors had been made using a highly sulfate-susceptible cement (e.g., one with 12.5% calculated C_3A), the expansion results, due to sulfate attack; i.e., ettringite formation, would have been as the authors' explanations of their data predict.

Additional References

10. Hansen, W.C. Attack on Portland Cement Concrete by Alkali Soils and Waters—A Critical Review, *Highway Research Record* **1966,** *113,* 1–32.
11. Binda, L.; Baronio, G. "Measurement of the Resistance to Deterioration of Old and New Bricks by Means of Accelerated Aging Tests," *Durability of Building Materials,* Elsevier, Amsterdam **1984,** *2,* 139–154.
12. Pepper, L. Unpublished work.