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Discussion

Reply to the discussion by William G. Hime and Stella L. Marusin of the paper "The distribution of bound sulfates and chlorides in concrete to mixed NaCl, $MgSO_4$, Na_2SO_4 attack"☆

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We will not respond in any detail to general criticisms of the analytical methods we have employed; we have already done so [1]. We do not agree with the view expressed by Hime and Marusin that the use of SEM to characterize concrete is unique. Indeed, several of the papers that appeared in the first issue of Cement and Concrete Research in 1970 relied on the use of scanning microscopy. In contrast with their views, one of the ongoing objectives in developing modern methods of analyses is to quantify the features of increasingly smaller volumes of materials. While compositional maps have their utility, they are not a substitute for analyses which combine the direct observations of microstructure with microanalyses of composition.

As Hime and Marusin are aware, we have also prepared montages containing up to 1000 individual SEM images. These have demonstrated the occurrence of sulfate attack over areas comparable to those which can be observed by optical petrography.

In the presence of sufficient sulfate, Friedel's salt converts to ettringite. We believe this is also occurring in the concretes of present interest. However, because the chloride remains within the concrete, it migrates to regions where Friedel's salt is stable. We explained the mechanism in the paper.

We had discussed the formation "magnesium silicates" in a previous paper [2]. Regardless of whether the assemblage discussed in the present paper is an intimate mixture of hydrous silica and brucite or magnesium silicates, the result should not be surprising. As hydrous silica and brucite are not compatible [3,4], their eventual conversion to a magnesium silicate should be anticipated. The fact that these compounds did not form as a glaze on the concrete surfaces facing the Mg source is an indication of the low quality of the concretes investigated. Surface coatings of these compounds are well-documented in marine structures. However, concretes for marine applications are typically produced at low water-to-cement ratios and, as a consequence, exhibit much lower permeabilities than the concretes we analyzed. Thus, brucite/hydrous silica/magnesium silicate deposits are typically observed near the concrete surfaces.

As Hime and Marusin show in their Figure 1, mica flakes are occasionally observed and have not confounded our analysis.

In the paper, we showed ettringite formation at a variety of locations. It can always be claimed that ettringite is a normal component of Portland cement concrete, as Hime and Marusin have done. However, it should be pointed out that, except in atypical locations, ettringite is consumed in AFm formation within a few days after mixing. We confined our analysis to regions where the ettringite observed had formed as a consequence of the ingress of external sulfate.

A comparison of the sulfate contents of Type III cements is not appropriate. This is for two reasons. Type III would not be used where sulfate resistance is desired. More importantly, because Type III is more finely ground, the interstitial phases have a higher surface area. This results in the incorporation of a higher proportion of sulfate based on the optimum gypsum test [5].

As with the suggestion that ettringite is a normal component of Portland cement concrete, it seems misleading to imply that ettringite should be present in 10-year-old concrete, because it may form when fly ash is exposed to a lime solution. We do not share in common the experience of routinely observing ettringite within fly ash particles when a mature concrete has not been subjected to the actions of sulfates.

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There may be a variety of sources of gypsum formation in concrete, but our observations of carbonated zones tend to indicate elevated sulfate paste contents as opposed to the formation of gypsum which can be readily identified as such.

Visual inspection of the in-place concretes we analyzed show the presence of efflorescence on their surfaces. In carrying out microstructural analyses, we occasionally observe deposits of sodium sulfate, as well as sodium chloride, within pastes. We agree with Hime and Marusin that these salts crystallize as solutions passing through the concrete reach evaporative fronts. Alternatively, we do not regard the sample preparation techniques used by us as flawed. Rather, it must be remembered that the drills used in coring the homes are water-cooled. Thus, salt dissolution from near-surface regions is likely.

References

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