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Discussion

A discussion of the paper "Durability of the hydrated limestone–silica fume Portland cement mortars under sulphate attack" by J. Zelić, R. Krstulović, E. Tkalčec and P. Krolo[☆]

John Bensted*, Juliet Munn

School of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E 7HX, UK

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Drs. Zelić, Krstulović, Thalcec and Krolo have obtained useful durability data in their studies of sulphate attack at ambient temperature. They studied the sulphate resistance of mortars containing Portland cement 45 and Portland cement 45 with 30 mass% ground granulated blastfurnace slag (ggbs), also each with condensed silica fume (csf) additions up to 15 mass% with and without ground limestone substituting for 15 mass% of cement. A sulphate-resisting Portland cement 45 was used as the base reference material. The mortars were stored in solutions of Na_2SO_4 and $MgSO_4$, each of which contained 0.26 mol/dm^3 SO_4^{2-} concentration. The mortars containing (a) no limestone and more than 5 mass% csf, (b) 15 mass% limestone and more than 2 mass% csf, demonstrated good sulphate resistance and lower expansions than the control SRPC 45 mortar [1].

The authors correctly attribute that csf, because of its active pozzolanicity, effectively reduces the leaching of lime and the amounts of both gypsum and ettringite formed by sulphate corrosion of the mortars and hence increases the durability of these mortars. Also, limestone is not an inert filler and actively participates in the hydration of the Portland cement, favouring the formation of the calcium monocarboaluminate hydrate ("monocarbonate") at the expense of the calcium monosulphoaluminate hydrate ("monosulphate") formed in normal Portland cement hydration. Both these latter hydrates have a hexagonal plate-type morphology and each contains extraneous ions in solid solution. Also, since the "monosulphate" and "monocarobonate" can themselves enter into solid solution with each other to a large degree, this facilitates the effective superseding of "monosulphate" by the more extensively formed "monocarbonate".

The lack of observed "monosulphate" $C_3(A,F)\cdot CaSO_4\cdot H_{12}$ is not altogether surprising in the hydration of the limestone containing cements. The change from ettringite to monosulphate during normal cement hydration is commonly incomplete [2]. When limestone is present the hexagonal prism-type phase (calcium tricarboaluminate hydrate $C_3(A,F)\cdot 3CaCO_3\cdot H_{30}$) is very unstable at ambient temperature and normally would not exist under these conditions. Hence, the hexagonal plate-type "monocarbonate" is the preferred phase formed. Because of the large level of carbonate present in the limestone containing cements relative to the cement sulphate content and the incompleteness of the ettringite to "monosulphate" reaction, the "monocarbonate" is predominantly formed. Any "monosulphate" produced would, as mentioned above, readily be engulfed in solid solution in the "monocarbonate" and would commonly not be independently detectable. Normal sulphate attack depends upon two main expansive reactions [3].

- Reaction of sulphate ions with calcium hydroxide to form gypsum.
- Reaction of gypsum with the monosulphate/C_4AH_{13} solid solution to form ettringite.

Since the second reaction would involve a solid solution mostly with carbonate and very little sulphate included, it cannot happen to any significant degree, because the hexagonal-type prism phase would be predominantly carbonate containing and thus unstable to the extent that it would probably not occur. Under these circumstances, the lack of this reaction would assist sulphate resistance, as no expansive reaction could arise. Furthermore, the other expansive reaction (reaction 1) would not take place to any significant degree, if at all, because the csf would effectively "mop up" the calcium hydroxide CH being formed, so the expansive conversion of CH to gypsum would not arise.

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* Corresponding author. Tel.: +44-207-631-6800; fax: +44-207-631-6803.

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The authors' conclusions [1] concerning the high sulphate resistance when limestone and csf are both present are upheld and in agreement with the earlier work by Piasta et al. [4]. They found that at ambient temperature Portland composite cement with limestone filler showed improved sulphate resistance and mechanical properties over Portland cement without the limestone addition. This improved sulphate resistance was attributed to the formation of "monocarbonate" instead of "monosulphate" and the calcium aluminate hydrates like C_4AH_{13}, with ettringite formed in normal cement hydration remaining unchanged.

However, at lower temperatures, below 15°C and particularly at 0–5°C, a different reaction scenario can arise, when the possibility of thaumasite sulphate attack can occur [5,6]. Here ground limestone can be a reactant in the slow conversion of the main hardened cement binder C-S-H into the non-binder thaumasite. Thaumasite $CaCO_3 \cdot CaSiO_3 \cdot CaSO_4 \cdot 15H_2O$ is a hexagonal prism-type phase similar to ettringite, with which it can enter into a partial solid solution that is often given the independent name of woodfordite. There are two thaumasite-forming reactions, which often occur together.

1. C-S-H reactions with gypsum, calcite and/or atmospheric CO_2 in the presence of Ca^{2+} ions in excess water.
2. Conversion of ettringite into thaumasite by reaction of ettringite with C-S-H, calcite and/or atmospheric CO_2 in the presence of Ca^{2+} ions in excess water.

These reactions are general at low temperatures and are very slow and can take many weeks to produce a significant yield. Once the temperature exceeds 15°C, the reaction ceases, but starts up again when the temperature again falls below ca. 15°C. The reaction is general in that any source of carbonate, silicate and sulphate in the presence of excess water and calcium ions can lead to thaumasite being produced. Thaumasite formation can be hindered and ideally prevented by reducing the permeability of the hardened cement, mortar or concrete. This can be achieved by incorporation of superplasticisers and/or extenders like csf, metakaolin, pulverised fuel ash (pfa) or ggbs in the mix [5]. So csf should militate against thaumasite production. It would be useful to extend the experiments undertaken to low temperatures, because the presence of ground limestone might encourage thaumasite to be formed as a mushy hexagonal prism-type solid in the presence of ingressing sulphate over a long period of time. The slowness of its formation is beneficial, in that once detected, any remedial action is normally straightforward to undertake. Stopping the flow of water or moisture through the hardened structure would seriously impede and maybe prevent its production at a level where remedial action to a hardened cementitious structure is deemed to be necessary.

In conclusion, the type of work undertaken by the authors is very valuable, but if lengthy very cold spells of weather are commonly encountered, then thaumasite sulphate attack could arise. Unlike conventional sulphate attack, thaumasite sulphate attack also attacks the hydrating alite C_3S and belite C_2S phases. In the past, thaumasite formation has sometimes been mistaken for ettringite sulphate attack. It is not commonly known to be a serious structural problem, but cement technologists need to be more fully aware as to how and where it can form. A recent UK government report discusses the present state of knowledge in this area [7], which is also available in a summarised form [8].

References

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