Pergamon

Cement and Concrete Research, Vol. 28, No. 12, pp. 1837–1838, 1998

PII S0008-8846(98)00150-1

DISCUSSION

DISCUSSION OF THE PAPER "DELAYED ETTRINGITE FORMATION: THE EFFECT OF TEMPERATURE AND BASICITY ON THE INTERACTION OF SULPHATE AND C-S-H PHASE" BY L. DIVET AND R. RANDRIAMBOLOLONA[1]

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(Received June 17, 1998)

In this very interesting paper the authors have drawn attention to some of the unusual characteristics of interaction between preformed C-S-H phase and SO_4^{2-} ion. In view of the importance of this interaction it is of interest to examine the results more closely to see if any further information could be garnered.

For the ease of presentation the salient features of the paper have been collected below:

1. C-S-H sample used had a BET specific surface of 350 m^2/g and thermoporometric surface of 320 m^2/g. The C/S ratio was 1.57.
2. Figure 3 shows that the fixation of SO_4^{2-} increases with increasing concentrations of both NaOH and the equilibrium SO_4^{2-} ion in solution, in the latter case at least up to 150 mmol/L concentration. The reported maximum fixed SO_4^{2-} is 2 mmol/g of C-S-H, i.e., 19% by weight. The fixation has been reported to follow the Langmuir isotherm.
3. Figure 4 shows that in a 2 M NaCl in 0.2 M NaOH solution, the sulfate fixation has increased to about 2.5 mmol/g of C-S-H, i.e., about 24% by weight.
4. Figure 5 shows that in 0.1 M NaOH solution, the sulfate fixation increased with increasing temperature at least up to 80°C. The maximum fixed SO_4^{2-} is 2.5 mmol/g C-S-H by weight in equilibrium solution of 175 mmol/L concentration at 80°C.

The fixation figures are rather high as the authors have already noted in the paper. The question that comes immediately in mind "Is this interaction unique for SO_4^{2-} ion or is it universal for all negative ions?"

The sulfate ion belongs to the regular tetrahedral BX_4 group of ions. In all ions of this group, B-X distance is about 1.5 Å irrespective of the nature of B. Incidentally, this S-O distance indicates that S-O bond is not ionic but a resonance bond (1). From the S-O distance the O-O distance could be worked out to be 2.45 Å and the radius of O as 1.22 Å. A fixed SO_4^{2-} ion on C-S-H surface can have two extreme configurations. It can either rotate around an S-O axis, thereby forming an inverted right cone with a base of 21.9 $Å^2$ area, or it can gyrate, forming a sphere of revolution with a diametrical plane of area 23.3 $Å^2$. A combined

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configuration also could be visualized. The calculated sizes are so similar that a mean value of 22.6 Å^2 could be used to garner information about the disposition of the fixation sites.

Disposition of the fixation sites on C-S-H in NaOH-Na_2SO_4 solutions at 25°C: From Figure 3 it can be seen that the maximum amount of fixed SO_4^{2-} is 2 mmol/g of C-S-H. The area needed for the fixed sulfate ions is given by 22.6•.002•N, where N is the Avogadro number. This comes out to be 272 m^2. From this area one can calculate the area occupancy to be 272/350 = 0.7777. This value is very near to the area occupancy of closest packing of equivalent circles or spheres on a square lattice, i.e., 0.785. The closeness of the above two values indicates that the fixation sites on C-S-H are distributed effectively on a square lattice.

Disposition of fixation sites at higher temperature or in the presence of 2 M NaCl solution: From Figures 4 and 5 it can be seen that, in each case, the maximum fixation is about 2.5 mmol/g C-S-H. The area needed by 2.5 mmol sulfate ion is 340 m^2 and the area occupancy is 0.971. This is higher than the area occupancy of closest packing of equivalent disks or spheres, i.e., 0.9069. It is obvious that in these cases, SO_4^{2-} ions are in a multilayer state and sites are more densely packed than in the previous case.

From the above it appears that the number of sites and their disposition depend on the ambient solution characteristics, i.e., on the concentrations of NaOH, NaCl, SO_4^{2-}, and temperature. From Figures 3, 4, and 5 it appears that the amounts of fixed SO_4^{2-} could be increased above the values reported by further increasing the concentrations of NaOH, NaCl, and SO_4^{2-}. (In a drying concrete NaOH concentration could easily go above 0.5 N.) All these in their turn indicate that some structural changes occurred in C-S-H during SO_4^{2-} fixation.

The following could be one of the possible structural changes that could have occurred. An examination of CaO-SiO_2-H_2O phase diagram shows that the C-S-H sample used is stable in about 16 mmol/L CaO solution. Any decrease in the ambient CaO concentration decreases CaO/SiO_2 of C-S-H. The liberated CaO will form gypsum. The authors have checked this possibility by taking x-ray diffraction diagram of treated C-S-H samples. However, their x-ray diffraction experiments might have been vitiated by the low bulk volume fraction of gypsum in the reacted solid and inhibition of crystal growth of gypsum by dissolved silica, another tetrahedral BX_4 ion. Electron microscopic and selected area electron diffraction techniques are better suited for the detection of low volume fraction components in any mixture.

Reference

1. R.C. Evans. An Introduction to Crystal Chemistry, p. 225, Cambridge University Press, Cambridge, 1966.