



Discussion

A discussion of the paper “Thaumasite formation in Portland–limestone cement pastes” by S.A. Hartshorn, J.H. Sharp and R.N. Swamy[☆]

John Bensted*, Juliet Munn

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

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Dr. Hartshorn, Prof. Sharp and Prof. Swamy have undertaken an important study at low temperature (2°C) on cylinders made at a water/solids ratio of 0.5 from Portland cement with 0%, 5%, 15% and 30% limestone additions that had been cured in water at ambient temperature for 28 days. These cylinders were then stored in various sulphate solutions at 5°C for periods of up to 420 days. The pastes containing fine limestone additions were found to be susceptible to formation of thaumasite after only a few months of exposure to sulphate solutions. Importantly, the degree to which thaumasite had formed was greater with increasing limestone additions and also when magnesium sulphate was present in the solution. This production of thaumasite was accompanied by formation of brucite $Mg(OH)_2$ and secondary gypsum $CaSO_4 \cdot 2H_2O$. In addition, portlandite, $Ca(OH)_2$, was observed to be a reactant rather than a reaction product and C–S–H gel was also consumed by the thaumasite-forming reaction [1]. Indeed, some thaumasite was found to be produced in Portland cement containing only 5% limestone filler [1].

In the European standard for common cements EN 197-1 [2], up to 5% ‘minor additional constituents,’ which can be finely ground limestone, are permitted to be ground into common cements. There are also two grades of Portland limestone cement that can contain respectively 6–20% and 21–35% ground limestone. Portland limestone cements are increasingly being used across Western Europe. For instance, in Italy Portland limestone cements now account for two-thirds of all construction cements produced, whilst in France they account for three-fifths of current cement

production. Interestingly, in France, Portland limestone cements are not normally recommended for use in below ground concrete structures and are commonly utilised in the construction of internal walls in buildings.

Long-term durability of structures containing Portland limestone cements is thus of great importance. The work carried out by the authors [1] has clearly demonstrated that Portland limestone cements should not be used where conditions for thaumasite sulphate attack arise [3]. After all, earlier work has shown that thaumasite (a nonbinder) can be formed as a general reaction from C–S–H binder, sulphate and carbonate in the presence of excess calcium ions and excess water below 15°C and particularly at 0–5°C [4–6]. Work done at the UK Building Research Establishment has highlighted how below ground concrete foundations (where the temperature commonly remains below ca. 10°C) can be susceptible to thaumasite sulphate attack when the concrete above ground remains unaffected [7].

Thaumasite is mostly formed in cement, mortar and concrete by the ingress of external sulphates in the presence of excess water. Sometimes thaumasite can be generated internally [8]. Where gypsum is already present in the system in contact with calcium carbonate or atmospheric/water-borne carbon dioxide in the presence of calcium ions, then a possibility exists for internal generation of thaumasite, particularly if excess water is regularly present in the hardened cement, mortar or concrete. Internally generated thaumasite is at present much rarer than thaumasite formed by external sulphate attack.

Fortunately thaumasite sulphate attack is slow to arise, so deterioration is gradual and not sudden, which allows sufficient time to undertake remedial work [3,8,9]. Thaumasite (a hexagonal prism type of phase) is readily recognised by its characteristic mushy acicular crystalline habit, which bears some resemblance to the hexagonal prisms of ettringite formed in the hydration of Portland cements and in

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* Corresponding author. Tel.: +44-208-698-9831; fax: +44-208-698-9831.

E-mail address: bensted.j@btinternet.com (J. Bensted).

¹ Tel.: +44-207-631-6800; fax: +44-207-631-6803.

sulphate attack upon Portland and high-alumina cements [10–12]. Indeed thaumasite and ettringite can undergo partial solid solution, where the phase is sometimes called woodfordite. One way for thaumasite to form is from ettringite via woodfordite [4–6]. Thaumasite obtained through sulphate attack upon cements, mortars and concretes tends to be less well crystalline than the naturally occurring mineral form, because (like ettringite in cementitious systems) it is impure as a result of containing extraneous ions in solid solution.

The paper discussed [1] is a valuable contribution to our knowledge of what can happen when Portland limestone cements are subjected to sulphate attack.

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