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Quantification of thaumasite in cementitious materials by $^{29}Si\{^{1}H\}$ cross-polarization magic-angle NMR spectroscopy

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The paper by Skibsted *et al.* on the quantification of thaumasite in cementitious materials is a useful contribution to our understanding of the nature and extent of thaumasite formation in cement.

Employment of $^{29}Si\{^{1}H\}$ cross-polarization magic-angle spinning nuclear magnetic resonance (CPMAS NMR) has enabled both qualitative and, more importantly, quantitative determination of thaumasite in cementitious materials. This technique reduces instrument time by up to a factor of 1000 over ^{29}Si MAS NMR due to the large difference in spin–lattice relaxation times for ^{1}H and ^{29}Si and to the ^{29}Si gain in intensity by CP for thaumasite. Between 2 and 15 wt% of thaumasite in five laboratory samples was clearly demonstrated, and it was felt that estimates of thaumasite as low as 0·5–1·0 wt% could be estimated if the cement samples have a low paramagnetic impurity content. Complementary work with ^{27}Al MAS NMR enabled quantification of ettringite to be obtained, but $^{13}C\{^{1}H\}$ CPMAS NMR was less useful than $^{29}Si\{^{1}H\}$ CPMAS for quantifying thaumasite. The important outcome of this work has been the very clear demonstration that thaumasite can be formed in cement materials using various sources of sulfates and carbonates, that large quantities of thaumasite can form in a virtually aluminium-free sample, and that because of the differences in geometries for the AlO_6 and SiO_6 octahedra in ettringite[1] and thaumasite[2] (which enable substitution of Si in ettringite for Al to give a different resonance from that found in thaumasite), thaumasite can be clearly quantified unambiguously in the presence of ettringite, which is not always the case with other techniques.[3]

I would agree with the suggestion by Skibsted *et al.* that ^{13}C MAS and CPMAS NMR may be useful NMR techniques in future studies of carbonation reactions in hardened Portland cements. Their observations of the CO_3^{2-} ion in thaumasite by $^{13}C\{^{1}H\}$ CPMAS NMR demonstrates the presence of ^{1}H in proximity to ^{13}C in accordance with the crystal structure and shows the existence of hydrogen bonds between hydrogen atoms in some of the water molecules and the oxygen atoms of the CO_3^{2-} ion is also of value. Such proximity facilitates charge delocalization away from the $[Si(OH)_6]^{2-}$ groups towards both the CO_3^{2-} ions and the H_2O molecules. In the absence of the CO_3^{2-} ions

and the H_2O molecules it is extremely unlikely that thaumasite with its $[Si(OH)_6]^{2-}$ could even form as a stable entity.

The increasing recognition that the non-binder thaumasite is a more common deterioration product of mortars and concretes than previously realized is one illustration of the importance of the work undertaken by Skibsted *et al.* Thaumasite had earlier been shown to be formed from the reaction in air of lime and silica, tricalcium silicate or β-dicalcium silicate with calcium sulfate, calcium carbonate and water at 1–4°C.[4,5] This indicated that its formation was not specific to any particular combination of constituent materials but needed a source of lime and silica (separately or combined), a source of carbonate (such as calcite or atmospheric carbon dioxide in the presence of Ca^{2+} ions) and a source of sulfate (such as gypsum, hemihydrate or anhydrite) in the presence of excess water. In the past, thaumasite was not commonly identified on account of its close similarity with carbonated ettringite, with which it is often confused.[3] Indeed, thaumasite and ettringite can and do form solid solutions with each other, although such solid solutions do not tend to go to completion. The solid solution of thaumasite and ettringite is sometimes given the independent mineralogical name of woodfordite.[6]

Thaumasite forms below 15°C, especially at about 10°C or less, ideally within the range 0–5°C, under cold, damp conditions. Once formed it is stable up to 110°C (without undergoing any lattice collapse), when it decomposes to form the disordered structure known as thaumasite glass.[3] Ettringite is not so stable, as often above 50°C it suffers from lattice collapse but not proper disorder, as manifested by its X ray diffraction pattern showing the lack of a crystalline lattice but its infrared spectrum revealing the presence of a similar waveband arrangement to that of ettringite.[7] However, above about 80–90°C true decomposition of ettringite manifests itself. Another peculiarity of thaumasite is that, unlike most other structures with SiO_6 units,[8] it is formed at normal pressures.[4] Thaumasite formation is irregular in that it only takes place when the temperatures are low. Such a reaction does not occur to any perceptible extent at about 20°C or above. The danger with its formation is that the principal cementitious binder calcium silicate hydrate C-S-H is gradually changed into a white powdery non-binder.

Why then does thaumasite, unlike ettringite, only form at lower temperatures? The answer appears to lie in the theoretical instability of the $[Si(OH)_6]^{2-}$ group present, since the key factor in the appearance of thaumasite seems to be the formation of $[Si(OH)_6]^{2-}$ groups that contain silicon in 6-coordination with OH^- ions.[9] The ionic radius of Si^{4+} is 0·42 Å, which is below the ionic radius for Ge^{4+} of 0·53 Å. The 6-coordination of Ge^{4+} by O^{2-} or OH^- is known, and is of much more frequent occurrence than the corresponding 6-coordination by Si^{4+}. Although 6-coordination of Si by O^{2-} or OH^- can be regarded as feasible on account of the closeness of the ionic radii and ionization potentials of Si^{4+} and Ge^{4+}, the smaller size of the Si^{4+} ion means that SiO_6 and $Si(OH)_6^{2-}$ units are strongly polarizing and would require special criteria for stability.[10]

Such criteria involve formation under special conditions such as appropriate charge delocalization by other atoms or groups present in the structure (such as carbonate) when formation arises at or near the atmospheric pressure.[10] The critical state for thaumasite formation is likely to be expansion of the coordination sphere of silicon, which would involve a considerable rearrangement of the basic silicate structure taking place. The intermediate transition which would occur as the coordination shell of silicon by OH^- is increased from 4 to 6 would, according to Kleber's coordination temperature rule,[11] be less likely to be stable at higher temperatures. Hence thaumasite formation would be favoured at lower temperatures, as is observed in practice, especially at about 0–5°C. Such formation is very slow, and is not simply a reaction of the dissolution and precipitation type but involves at least some measure of chemisorption.[10,12]

Thaumasite exists as acicular crystals, with a structural framework consisting of columns having the composition $\{Ca_6[Si(OH)_6]_2 24H_2O\}^{8+}$ oriented along the Z or prism axis and $[(SO_4)_2(CO_3)_2]^{8-}$ groups distributed throughout the intercolumnar channels. The structure is very similar to that of ettringite, and substitution of Si for Al within the columns and interstitial replacement of both CO_3^{2-} and SO_4^{2-} groups by SO_4^{2-} and H_2O results in a solid solution between the two minerals.[13] The solid solution is not totally extensive, because both thaumasite and ettringite can occur together as discrete end-members.[14] In cementitious structures, thaumasite, like ettringite, is not pure, and contains other ions in solid solution.[10] It has been pointed out that with regard to the destruction processes affecting cement pastes in sulfate media, above 20°C the formation of ettringite is decisive, while below 10°C the formation of thaumasite increasingly plays a determining role – not only is control of transformations in the aluminate phases a necessary condition for avoiding destructive sulfate attack, but at lower temperatures the control of transformations in the silicate phases is also necessary.[15] Also, even at ambient temperature, cements with high C_3S levels (above 60%) have been found to be more prone to sulfate attack than those with lower C_3S content, when both types have relatively low C_3A contents; for better sulfate resistance, C_3S and C_3A should both be addressed.[16] These two points are very important for sulfate-resisting cements in sulfate attack situations.[17]

Work at the UK Building Research Establishment[18]

has confirmed earlier work[4,5,19,20] that the formation of thaumasite is a general reaction occurring at low temperatures from the breakdown of the calcium silicate hydrate C-S-H in the hardened cement paste in the presence of an available supply of SO_4^{2-} and CO_3^{2-} ions. Studies of some case histories[18] have shown that if the C-S-H reacts with SO_4^{2-} and CO_3^{2-} ions under cold and wet conditions, thaumasite formation will be initiated and will continue to completion provided that external conditions do not change. Thaumasite does not need Al^{3+} ions or ettringite to be present in order to form. However, thaumasite can form through ettringite because of the solid solution and structural similarity, and if formed plentifully can effectively 'consume' ettringite by engulfing it and leaving none to remain. Also, thaumasite was found to form in sulfate-resisting Portland cement and when a calcareous aggregate had been used where the conditions of deterioration favoured its formation. Skibsted *et al.* have also observed formation of thaumasite when oolitic limestone aggregate is present. A further important observation in these studies[18] was that large amounts of thaumasite had been detected in foundation concretes without any evidence of structural damage above ground, which means that similar problems exist elsewhere and hitherto have gone unnoticed.[18] The thaumasite form of sulfate attack can be accompanied by swelling of expansion of the affected concrete, and added problems of freeze–thaw probably contribute to the degradation process.[18]

In the European pre-standard for common cements[21] the new SO_3 limits for CEM I, II, IV and V cements of strength classes 32·5, 32·5R and 42·5 and 3·5%, and for strength classes 42·5R, 52·5 and 52·5R as well as for all classes of CEM III cements are 4·0%. This trend towards higher SO_3 levels for many cements and the inclusion of up to 5% of filler material which can be calcareous, plus the inclusion of two classes of Portland limestone cement (containing 6–20% and 21–35% limestone, respectively), means that the propensity for thaumasite to form in mortars and concrete at low temperatures is increased. However, this propensity need not be a problem or indeed a reality. Thaumasite only forms when the reaction conditions are cold enough. When they are warmer, the reaction effectively ceases. Also, if low water/cement ratios are employed in the mix, internal transport of the requisite ions to produce thaumasite from all its constituents under cold conditions is frustrated. Should only small amounts of thaumasite form in a given area of mortar or concrete, if the overwhelming surrounding mass of the hardened cement paste remains as C-S-H, there should be no actual problem. Good-quality mortar or concrete is the practical solution for cement-based structures in such environments.

Considerations of all these implications shows that the work by Skibsted *et al.* is an important development for reliably quantifying thaumasite independent of ettringite using $^{29}Si\{^1H\}$ CPMAS NMR spectroscopy, which should lead to a greater awareness of the undesirability of the presence of large amounts of thaumasite in mortar and concrete, and hence encourage good engineering practices that can effectively deal with any potential structural risk. Their work has also produced some useful structurally related information on thaumasite, which helps us to understand more fully the precise nature of this increasingly important deterioration product of sulfate attack within hardened mortar and concrete.

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