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Cement & Concrete Composites 25 (2003) 805–807

Cement & Concrete Composites

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Guest Editorial

Thaumasite in Cementitious Materials

It is with great pleasure that we (as guest editors) introduce this and the following issue of Cement and Concrete Composites, which contain many of the papers presented at the 1st International Conference on Thaumasite in Cementitious Materials which took place in June 2002.

The special form of sulfate attack associated with thaumasite (designated in most of these papers as the thaumasite form of sulfate attack or TSA) can lead to particularly severe deterioration in concrete; in extreme cases the portions of a concrete member affected can lose all of its strength, and even fluidize—i.e. transform itself to a moist incoherent mass. TSA deterioration can be much more severe than conventional forms of sulfate attack as it is associated with the deterioration of the calcium silicate hydrate (C–S–H) gel, the main binding phase of the cement.

Thaumasite is an ettringite analogue; i.e. an AFt compound, containing silicate ions occupying the sites normally associated with aluminate, and carbonate ions in some of the sites normally associated with sulfate ions. It can be produced in concrete as a minor secondary reaction product without necessarily inducing the severe deterioration associated with TSA.

As stated previously, TSA is a special form of sulfate attack, and like conventional sulfate attack, it takes place in the presence of sulfate-bearing ground waters. In the more conventional forms of sulfate attack, ettringite is the primary component formed, and most of the damage is considered to be associated with expansion and cracking induced by its formation. The amount of ettringite that can form is limited by the alumina content of the cement. However, additional forms of damage can occur in permeable concretes with exposed evaporative surfaces. Internal damage is often induced by dissolution of calcium hydroxide and partial decalcification of C–S–H caused by long-continued passage of sulfate-bearing ground water through the concrete. Some local damage induced by crystallization of various salts near the evaporative surface may also occur.

In stark contrast to this limited damage potential for conventional sulfate attack, TSA damage is in principle unlimited. Unlike ettringite, the amount of thaumasite that can be formed is not associated with, and thus not limited by, the alumina content of the cement. Thaumasite can continue to be formed as long as external sulfate and carbonate sources continue to be available. The needed silica is supplied by the C–S–H itself, and if the reaction proceeds indefinitely all the C–S–H in a given concrete member can be totally destroyed.

The occurrences of minor amounts of thaumasite in concretes and mortars had been occasionally reported in the past, but it was not until the discovery of severe TSA in a number of deteriorated bridge foundations on the M5 motorway in Gloucestershire, UK in 1998, that the significance of this potential deterioration mechanism became widely recognized. Subsequently, reports of occurrences of thaumasite and of TSA developing in sub-surface structures in various countries have steadily increased.

It is highly appropriate that the 1st International Conference on Thaumasite in Cementitious Materials was held at the Building Research Establishment, UK, where many of the early occurrences were researched and documented. The Conference provided a timely opportunity for investigators to report their findings in a number of projects begun after the 1998 discoveries, and it provided a forum in which academic researchers, concrete practitioners, structural engineers and government representatives could discuss the growing body of information on TSA and its implications for construction practices.

The Conference featured more than 60 papers, and was began with an introductory paper summarizing TSA and thaumasite formation by Crammond. The papers contributed include reports of field occurrences, laboratory-based or mechanistic studies, and coverage of various related matters.

A number of papers reported on case studies in the UK, where much of the impetus on investigation of TSA has occurred, but it is clear that TSA (or at least findings of significant amounts of thaumasite in concrete) is to be found in many other places as well. These include occurrences described from various countries on the European continent, from North America, and from South Africa.

0958-9465/$ - see front matter
doi:10.1016/S0958-9465(03)00165-3

It may be that the future exposition of the geographical distribution of TSA may follow a pattern similar to that exhibited many years ago by reported occurrences of alkali–silica reactions (ASR). ASR was identified initially in one country (the USA) and studied extensively there. It was later recognized as a problem in Denmark and in a few other isolated places. Subsequently, as the diagnostic symptoms of ASR became more widely recognized and analytical methods more clearly defined, reports of ASR eventually appeared from nearly every country where concrete is produced and studied.

Such nearly world-wide distribution is possible, but not necessarily to be expected with TSA. In part, the geographical extent of TSA problems could be limited by the association of thaumasite formation with low temperatures (i.e. temperatures below 15 °C), which has been reported many times. Nevertheless, this association has apparently not precluded thaumasite formation (and possible future TSA) in places not generally considered to be cool-climate locations, such as South Africa and Southern California.

Not all of the occurrences reported involve concrete; reports on affected masonry mortars, tunnel linings, and other thin cement-based products exposed to external solutions are also prominently featured.

The sources of the carbonate ions involved in thaumasite formation are varied, but concern has been expressed by many that deliberate addition of finely-ground limestone to cement may contribute to possible future thaumasite-related problems. A number of reports of laboratory studies of effects of limestone-filled cements on the development of TSA are included in these special issues.

The first phase-pure laboratory preparations of thaumasite are also reported, along with more theoretical papers describing such features as multi-phase models of phase compatibility and solid solution characteristics in the thaumasite–ettringite system. Several papers describe proposed formation mechanisms and the importance of aluminium in 'catalysing' thaumasite formation. The implications of using silica-bearing supplementary cementitious materials on thaumasite formation in cement systems is also addressed by several authors.

A number of papers describe various analytical methods for the identification and quantification of thaumasite in affected concretes including applications of electron microscopy, optical microscopy, electron probe microanalysis, ^{29}Si NMR spectroscopy and stable isotope ratios.

In retrospect, it would seem that the conference focused on five key questions:

- What variation in thaumasite composition can be expected in concretes?
- What factors favour the formation of thaumasite?
- Can a distinction be drawn between physical and chemical effects?
- Can these observations define a mechanism for thaumasite formation?
- Can this knowledge be used to effectively inhibit TSA in the future?

The research presented has gone a long way toward addressing these questions.

For example, the degree of solid solubility in the ettringite–thaumasite system clearly impacts the accuracy of phase identification. Misidentification of thaumasite as ettringite in the past may have led to previous cases of TSA being misdiagnosed as conventional sulfate attack. Quantitative assessment of thaumasite is also rendered difficult. As a special consideration, octahedrally coordinated Si is not only a major component in thaumasite but also can be found in Si-substituted ettringite, thus potentially confounding interpretation of data from analytical techniques sensitive to octahedral Si. The extent of possible damage to be expected when Si-substituted ettringite (as distinct from thaumasite) forms in concrete is still uncertain. Whilst thaumasite can be formed in the absence of aqueous aluminium (as reported e.g. by Nobst and Stark), dissolved aluminate species clearly exert a stabilising role on AFt formation in general, and may be important in the ettringite (or woodfordite) precursor route emphasized by Bensted. The relative phase distributions associated with temperature variation and the consequent availability of thaumasite constituent species, e.g. CO_3^{2-} and SO_4^{2-}, are also central in defining thaumasite stability.

A significant debate surrounds the question of the importance of acid formation by oxidation of backfill materials as a stage in TSA. The question was raised in the UK Government Thaumasite Expert Group Report (UK Department of Environment, Transport and Regions: London, 1999). It has now been shown that thaumasite itself is unstable under acid conditions. This inconsistency may only be apparent, however. Acid-induced leaching can act to progressively expose new sites for subsequent TSA when and if alkalinity is subsequently restored by the buffering potential of the cement.

A number of the papers stress the importance of knowledge transfer from 'laboratory to practice'. Several papers discuss the implications of field and laboratory studies to recognition and classification of exposure sites with respect to the likelihood of future TSA damage, and to the modification of construction specifications to take account of such possibilities.

It appears that no single set of concrete parameters and environmental conditions defining the conditions under which TSA damage can be expected to occur can be established. Indeed, the "bulk" or average conditions within a concrete may not be important. Concretes are typically inhomogeneous, and local properties (e.g. at surfaces in contact with ground water) may deviate significantly from bulk properties. Nevertheless, the 'right' conditions for the development of TSA must involve local chemistry of both the concrete at the affected surface and the surrounding soil water (including pH, ionic composition and speciation); transport properties both within and external to the concrete; and various factors which define and influence reaction kinetics. All are linked to each other, and add to the difficulty of providing a positive answer to the final question posed, i.e. 'can this knowledge be used to effectively inhibit TSA in the future?'.

We recommend these papers, which represent a substantial background of research, as a basis for interested readers to arrive at their own answers.

All of the papers included in these two special issues of Cement and Concrete Composites were subject to rigorous peer review, and we are grateful to Professor Swamy for the opportunity to have them published in archival form.

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