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Discussion

A discussion of the review paper "Sulphate attack research—whither now?" by M. Santhanam, M.D. Cohen, and J. Olek[☆]

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Abstract

The review paper produced by Drs. Santhanam, Cohen, and Olek [Cem. Concr. Res. 31 (2001) 845.] is a thoughtful attempt to look at the current sulphate attack situation from the North American viewpoint. The review gives suggestions about what needs to be done to obtain more information about precisely how sulphate attack takes place in different situations. Also discussed is how test procedures may need to be modified to give data that are more representative of field situations, and the need for better modelling systems for sulphate attack. However, there are numerous points concerning the current situation that also need to be addressed in order to ascertain more clearly exactly what is taking place. These are discussed briefly below. © 2002 Elsevier Science Ltd. All rights reserved.

1. Geographical spread for sulphate attack

The review discusses the North American scene, including that of California with regard to sulphate attack. On the international level there is little specific mention or references to work done on sulphate attack in areas of the world unconnected to the American scene, such as in Europe.

A great deal of work has also been done outside of North America over the years, including Europe. There is a lot of information available in the general technical literature concerning sulphate attack in numerous countries. The effects of different cations upon sulphate attack has been known for a long time, but not perhaps in great mechanistic detail [2–4]. When thaumasite forms at low temperatures, below 15 °C (and especially at 0–5 °C), these are not *exceptional circumstances*. Such temperatures are not uncommon in Northern Europe and in parts of the USA (like Alaska and New England in wintertime) and Canada. Thaumasite has indeed been extensively studied before, but mainly outside of North America, such as in Europe and particularly the UK. Mechanistic information is already available about various forms of sulphate attack, but, as in many other areas of research, we still need to know more.

2. The role of scanning electron microscopy (SEM)

Firstly, the question of utilising SEM with energy dispersive elemental analysis (EDS) as a principal investigative tool needs to be addressed.

Marusin [5] has written an excellent paper on the pitfalls involved in SEM with EDS analysis. She has indicated how the size of the analysed area plays an important role and how failure to understand the cementitious systems and the instruments' capabilities can lead to misleading and erroneous conclusions. She also points out that for correct interpretation of the obtained data, a good geological background and a knowledge of cement chemistry is needed. Also, in the case of failure investigation, SEM studies should be considered as an adjunct analysis following petrographic observations and engineering evaluations of the particular structure.

Hime and Marusin [6] have also made some important points. In response to a paper by Brown and Doerr [7], Hime and Marusin argued that they used EDS spectra to imply significant formation of compounds due to influx of "aggressive species." Hime and Marusin [6] reported that Brown and Doerr had reported unbalanced chemical equations, had ignored the facts that the EDS analyses represented the elemental concentrations within a volume of less than one-trillionth of a cubic inch, and that the elements may not indeed indicate the phenomena or the compounds they represent them as.

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The Hime–Marusin view was that no classic evidence of sulphate attack had been found in any of these homes. Rather than surface layers of gypsum or ettringite, what was found was thenardite and mirabilite, provided that the stress was due to their concentrated solid solution, proving that the distress was due to "salt hydration distress," i.e., the destructive conversion of thenardite to mirabilite. Hime and Marusin [6] also disagreed with Brown and Doerr when the latter had reported that the formation of sodium sulphate on a structure is an indication of sulphate attack occurring in the interior of that concrete. Hime and Marusin [6] mentioned that it was no such thing, but rather a result of that salt wicking up the concrete surface after having dissolved every morning when the water sprinklers were turned on. Also, they reported that the linear appearance of this efflorescence, occurring about 2 in. (5.08 cm) above the soil, demonstrates this and can be shown in the laboratory. They particularly deplored the lack of optical petrographic evidence for sulphate attack.

In their reply, Brown and Doerr [8] considered the majority of the Hime and Marusin comments to be irrelevant to the content of their paper. This response can be regarded as being contentious, because the points raised are not *irrelevant* but *central* to the main thrust of the argument. Brown and Doerr [7] claimed to have found thaumasite, although Hime and Marusin [6] reported their finding no classic evidence of sulphate attack in virtually any of the Californian homes described. Rather than surface layers of gypsum or ettringite, what was found (at least by those not using techniques like thin sections that remove the evidence) was thenardite Na_2SO_4 and mirabilite $Na_2SO_410H_2O$, proving that the distress was due to "salt hydration distress," that is the destructive conversion of thenardite to mirabilite [6].

Hime and Marusin [6] also mentioned that Brown and Doerr had given erroneous chemical equations and in addition depended upon vanishingly small areas and volumes, as well as ignoring the lack of any optical petrographic evidence for sulphate attack. The comment by Brown and Doerr [8], that Hime and Marusin can contrive to produce claims of EDS spectra similar to those presented, does not satisfactorily deal with the specific points made by them.

I have used SEM extensively in my work, but, with the exception of one or two oilwell cementing failure investigations, have never considered it to be a prime research tool. Cement and concrete research studies are often very complex and need the application of numerous techniques, all of which have their particular advantages and shortcomings. The situation can be likened to each individual technique being part of a jigsaw puzzle, and the more techniques that you can use, the more pieces of that jigsaw you can put in place with certainty.

For example, in establishing the main cause of setting in Portland cements as being due to the onset of C-S-H formation, a wide range of techniques, including SEM (with EDS analysis) were utilised. However, SEM proved to be a useful supplementary technique that complemented the information given by the other experiments. In no way could reliable interpretations of the causes of Portland cement setting based on the use of this technique alone have been made [9].

SEM has been useful in investigating improperly set Class G oilwell cement in downhole situations. For example, it can clearly show drilling mud contamination of the cement, because there are major differences in morphology between drilling mud constituents and cements. SEM can be and has been appropriate for this type of examination, which is very different from the sulphate attack scenario. In one investigation [10] for instance, the presence of mica and barium sulphate amongst the cement grains showed evidence of extensive contamination of the hydrating cement slurry by residual drilling mud. Mica had been used as a lost circulation controller and barium sulphate as a heavyweight additive with drilling mud for seeking to ensure efficient mud circulation downhole. The clear-cut differences between the cement hydration products and the drilling mud chemicals allowed SEM to be employed usefully in this type of investigation.

Investigations of electron microscopy by Möser and Stark [11] have drawn attention to the shortcomings of SEM investigations of concrete attack. They have a high-resolution environmental SEM (ESEM) with a field emission gun (FEG), which can be operated both in the ESEM mode and as conventional SEM. A resolution of better than 2 nm is achieved in both types of operation. ESEM–FEG enables specimens to be protected from drying out and dehydration so that SEM and electron probe microanalysis can be carried out on building material samples in the original undistorted state in an unchanged environment. Their investigations had shown that ESEM–FEG was suitable for following morphological, physical, and also, where applicable, chemical changes.

Möser and Stark [11] also mentioned that previous investigations carried out with SEM have been based on special multistage preparative methods, which are extremely expensive both in terms of time and apparatus. Since the individual preparative stages take place "anonymously," during the sample investigations there is no certainty whether, after a series of preparative stages, the "true" specimen structures are being observed and analysed, or what specimen changes (artefacts) are caused by the preparation. In principle, it is also impossible by conventional electron microscopy to follow in situ the dynamics of dissolving, crystallisation, rearrangement, and reorganisation processes in which fluid media are involved. In situ investigations also require uncoated samples.

Conventional SEM can cause changes to the microstructure because of the high vacuum [11]. The microstructural components of concrete react in very different ways to vacuum drying. With water being combined chemically, adsorptively, or existing free in the capillary pores and voids during cement hydration, tensile forces leading to drying shrinkage (and thus to cracking and the widening of existing cracks) can arise when the system becomes dried under high vacuum. In alkali–silica reaction (ASR), new cracks can occur in the alkali silicate gel. Significant cracking is found with SEM for secondary ettringite formation from the high vacuum. Also, the ettringite can lose about $20H_2O$ of the $31-32H_2O$ water molecules originally present. The morphology of C-S-H can also be affected by the high vacuum.

For all the aforementioned reasons, other techniques should be applied to elucidate what is actually happening during sulphate attack. Optical microscopy is very important here, and X-ray diffraction, thermal analysis techniques, and infrared spectroscopy can also have a useful part to play. SEM should therefore be used in conjunction with other techniques and not as a prime investigative tool in sulphate and other concrete attack examinations.

Interestingly, one of the original papers that discussed the Southern Californian situation identified gypsum, ettringite, and sometimes birunite. This work utilised X-ray diffraction as the prime investigative technique and not SEM [12].

3. Decalcification

The term 'decalcification' is increasingly being applied in instances of magnesium sulphate attack in particular. This term conveys the impression that when C-S-H is being attacked, such as by magnesium sulphate solutions, CaO is directly replaced by MgO and the magnesium silicate hydrate formed has no binding capacity. Also, the impression is conveyed that the CaO content in the C-S-H gel is somehow inherently unstable. The observations that C-S-H has been found in historic structures in the Mediterranean area several thousand years old does not suggest that the CaO content of C-S-H is somehow unstable. Also, MgO can substitute for CaO in the Portland cement phases, including alite C_3S and belite C_2S. This 'decalcification' does not affect the hydraulicity of these phases adversely. Quite the opposite happens. Mg^{2+} and the other ionic forms found in solid solution in the main silicate phases decrease the thermodynamic stability, which increases the binding capacity due to the presence of unsatisfied surface forces. In other words, this kind of 'decalcification' is beneficial for hydraulicity and compressive strength.

'Silicate debonding' is a more useful term to apply instead of 'decalcification' in situations like magnesium sulphate attack. The Mg^{2+} ions cause the break-up of the C-S-H, which leads to an amorphous silica that can gradually react with the Mg^{2+} ions to form magnesium silicate hydrate that has no binding power and is thus deleterious to concrete structures. The cause of the deleterious attack is the silicate debonding caused by the Mg^{2+} ions and not any simple substitution of MgO for CaO within the C-S-H binder. This is related to the low magnesium hydroxide solubility and its saturated solution having a pH of only around 10.5, which is lower than the pH needed to stabilise the C-S-H. Accordingly, the silicate structure becomes denuded in liberating lime to the solution phase to establish its equilibrium pH:

$$Ca_3Si_2O_73H_2O + xH_2O \rightarrow 2\{SiO_2 \cdot x/2H_2O\} + 3Ca(OH)_2.$$

With magnesium sulphate effectively present, the lime reacts to form magnesium hydroxide (brucite) and calcium sulphate (gypsum):

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow Mg(OH)_2 + CaSO_42H_2O.$$

This reaction can proceed to completion because of the pH fall to ca.10.5. Silica gel, which lacks binding power, is left behind and can react very slowly with the magnesium hydroxide to form magnesium silicate hydrate. This basic mechanism for magnesium sulphate attack has been known for a long time [4].

Bonen and Cohen [13] have studied magnesium sulphate attack and consider from the mass balance aspect that the material $2MgO \cdot SiO_2 \cdot xH_2O$ is more likely to arise, which I would agree with [14]. The disintegration of the C-S-H gel during the $MgSO_4$ attack is a manifestation of the silicate debonding referred to above.

4. Use of modelling

Santhanam et al. [1] emphasise the importance of the different criteria used for modelling sulphate attack. They suggest that the parameters used, which include expansion and strength loss, need to be unified to develop successful modelling criteria.

The use of modelling needs to be applied with caution. There must be sufficient data available and an appreciation of interactive effects to make the models reliable. Modelling cannot be a substitute for real experimentation. It needs to be a supplement to it in order to deliver the goods. Certainly the modelling of deterioration processes should be encouraged and checked against field data. Reliable information needs to be fed to make the model useful in practice.

5. General information about sulphate attack

Skalny and Marchand [15] have pointed out that sulphate attack is not very common and that most mechanistic aspects are quite well explored. They also state that formation of ettringite or gypsum or thaumasite does not per se necessarily cause expansion. Even if in some cases expansion does occur, it does not necessarily lead to cracking or significant damage to concrete.

These authors [15] also state that it is difficult to develop accurate, reliable, and reproducible test methods and standards for deterioration processes like sulphate attack. Not least is the problem of obtaining sufficient reliable data when there are so many disagreements about techniques and mechanisms in order to move forward in a coherent manner.

It is very important not to regard the mere presence of ettringite as being a symbol of sulphate attack. In practice, only a minority quantity of the aluminate phase for instance reacts with gypsum to form ettringite [16]. This probably explains why pure preparations of ettringite are best obtained by reacting CaO or $Ca(OH)_2$ with aluminium sulphate in the presence of excess water [17] rather than reacting pure preparations of C_3A with gypsum in the presence of excess water. Also, much ettringite forms in the first few minutes during Portland cement hydration, when the cement–water mix is still very plastic and thereafter increases at a significantly slower rate [18,19]. Most of the sulphate in Portland cement hydration does not react with the aluminate or ferrite phases, but enters the C-S-H being formed [20]. Around 70–80% of the sulphate is ultimately present in the C-S-H phase. Furthermore, the ettringite to monosulphate conversion is often incomplete and ettringite from aluminate and ferrite phase hydration may remain unconverted as such within the hardened cement in the long term.

Importantly, earlier work by Copeland et al. [21] that showed ettringite could persist in 10-year-old pastes (and thus apparently indefinitely) in some Portland cements appears to have been forgotten or overlooked in a number of recent investigations.

Thaumasite sulphate attack (TSA) has been extensively studied [22–29]. A clear differentiation has been made between thaumasite formation (TF) and TSA, since not every occurrence of thaumasite is actual or potential sulphate attack [22]. Thaumasite has created problems in Europe at temperatures below 15 °C. The key to thaumasite being formed and its stability depends upon the stabilisation of the $[Si(OH)_6]^{2-}$ octahedral groups. Claims that thaumasite has formed in Southern California at more elevated temperatures are at present unconfirmed because this work was undertaken using SEM with EDS analysis as the prime investigative technique [6]. This work needs to be investigated using optical microscopy and also, if appropriate, X-ray diffraction and other suitable techniques as well.

Criteria for stabilising TF for permitting its possible existence at elevated temperatures has been given [28]. There needs to be sufficient pressure, and this might include crystallisation pressure, to stabilise the octahedral arrangement of hydroxyl groups by silicon for thaumasite to form. Once produced, thaumasite has a better temperature stability than ettringite, being stable up to ca. 110 °C. Thaumasite only occupies around 45% of the volume of ettringite that it is derived from via the woodfordite route. Therefore, its expansive capability is much less than that of ettringite [29].

Birunite $8.5CaSiO_3 \cdot 8.5CaCO_3 \cdot CaSO_4 \cdot 15H_2O$ [28,30], which has been mentioned as a product of sulphate attack in California [12], needs to be further characterised. As with thaumasite, SEM with EDS analysis cannot be regarded as confirmatory for positively identifying this mineral [6]. Modern X-ray crystallographic and diffraction studies of birunite should also be undertaken to establish an up-to-date base for birunite. Also, birunite needs to be synthesised and its relationship with thaumasite more closely explored, so that if it does have a definitive role in sulphate attack, then this can be suitably assessed.

Delayed ettringite formation (DEF) has been widely studied (e.g. Refs. [31–38]). There has been much and often contradictory data generated in the technical literature on this subject. The general consensus is that this is a weak form of sulphate attack and is often found growing in cracks and voids already present. Fine cracking has been known for a long time—it has been called *thermal cracking* and is a well-known *physical* effect that arises when too much heat is generated during curing. However, thermal cracking is not always a distinct *chemical* problem per se and certainly not one attributable solely or even mainly to DEF. C-S-H formation can also have a part to play at times with thermal cracking along with ettringite. Diamond [36] postulates about *the potential massive formation of ettringite that drives DEF-induced deterioration ordinarily remains latent*. From the aforementioned comments on ettringite, it is unlikely that there is any potential massive formation for this mineral.

Finally, the questions of concrete attack (including sulphate attack), concrete distress, and efflorescence need to be addressed when considering what sulphate attack actually is.

Efflorescence is not normally a form of concrete attack. It is usually merely unsightly and does not normally affect the structure adversely [39,40]. The thenardite-to-mirabilite reaction cycle is by its very nature an efflorescence reaction, as mentioned earlier. It is not really sulphate attack per se, although it can be an eyesore and sometimes gives rise to spalling from the expansive formation of mirabilite, but has not been a known cause of loss in structural integrity so far.

Also, a recent paper by Famy and Taylor [41] has dispelled numerous myths and uncertainties concerning ettringite that have become increasingly promulgated in recent years. I am overall in broad agreement with what they are now saying [41], viz.:

- Ettringite persists indefinitely in the hydration products of many Portland cements and is commonly observed in field concretes regardless of the occurrence of damage or the curing temperature.
- Cracks at aggregate interfaces or elsewhere are a feature of stress, but the presence of ettringite in them is not an indicator of distress.
- Assuming that the total SO_3 content of the cement is within normal limits and that there is no other source of sulphate, damage from ettringite formation has been shown only to occur in some materials that have experienced temperatures greater than 70 °C.
- Any damage resulting from ettringite formation is probably due to growth within the paste of crystals

that are too small to be detectable by petrography or SEM. Larger crystals of ettringite (for example, 10–30 μm long), observable in cracks or voids by these methods, are formed by recrystallisation in both damaged and undamaged concretes, and may result from damage but are not its cause.

- There is no sound basis for claims that damage from DEF can occur in concretes that have not been subjected to an elevated temperature, if the case of cements having substantially higher total SO_3 contents than those allowed by normal specifications is excluded. Equally, there is no sound basis for the view that slowly reacting sources of SO_3 in the clinker or cement are a potential cause of damage.

The review by Santhanam et al. [1] usefully addresses a whole range of problems associated with sulphate attack research. However, as pointed out in this response, there are other issues that merit attention in order to progress sulphate attack research. These include sorting out the best investigative techniques to use and having more extensive coverage of the technical literature worldwide, so that researchers in general have a much better idea of what is or is not known about sulphate attack from the viewpoints of the chemistry and engineering properties. We do not want to keep 'reinventing the wheel' in these respects! There is a 'good side' to ettringite in its role of smooth set regulation [9,41,42] and this should not be forgotten either. The mere presence of ettringite, as aforementioned, is not per se an indication of trouble. Closer investigation is always needed for verification of what happens in particular situations.

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