UNIVERSITY OF LEEDS

This is a repository copy of *Current knowledge of external sulfate attack*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/84114/

Version: Published Version

Article:

Whittaker, M and Black, L (2015) Current knowledge of external sulfate attack. Advances in Cement Research. ISSN 0951-7197

https://doi.org/10.1680/adcr.14.00089

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

White Rose
university consortium
Universities of Leeds, Sheffield & York

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

Advances in Cement Research

Current knowledge of external sulfate attack
Whittaker and Black

Advances in Cement Research
http://dx.doi.org/10.1680/adcr.14.00089
Paper 1400089
Received 24/10/2014; revised 24/11/2014; accepted 11/12/2014

ICE Publishing: All rights reserved

Current knowledge of external sulfate attack

Mark Whittaker
PhD student, Institute for Resilient Infrastructure, School of Civil Engineering, University of Leeds, Leeds, UK

Leon Black
Associate Professor, Institute for Resilient Infrastructure, School of Civil Engineering, University of Leeds, Leeds, UK

This paper offers an update of the current understanding of sulfate attack, with emphasis on the sulfates present in an external water source percolating through, and potentially reacting with, the cement matrix. The paper considers the explanations put forward to explain sulfate attack, both from a chemical and microstructural perspective. Similarly, this paper reviews work on the physical damage caused by the precipitation of sulfate salts in porous materials. With the increased use of binary and ternary blends, this paper also considers the impact of binder composition on sulfate resistance, and similarly reviews how the nature of the sulfate species can affect the nature and extent of any deterioration. This then leads on to the important consideration of differences between field- and lab-based studies, reviewing the effect of various experimental parameters on sulfate resistance. This latter topic is of great importance to anyone who wishes to carry out such experiments.

Current knowledge of sulfate attack

Simply put, sulfate attack encompasses a series of chemical and physical interactions that occur between hardened cement paste and sulfates. Although sulfates already present in cement, often as gypsum to prevent flash set, may, depending on curing conditions, cause damage in the form of expansion and cracking in the form of delayed ettringite formation (Collepardi, 2003; Taylor *et al.*, 2001), this is not the focus of this review. Rather, this paper covers the deleterious impact of external sources of sulfate on cement paste, and therefore concrete.

Groundwater is a natural sulfate source to which buried concrete can be exposed. These waters typically have a low sulfate content; a fact recognised in standard BS EN 206:2013 (BSI, 2013). The more severe class with respect to sulfate attack (class XA3) fixes the concentration of SO_4^{2-} between 3000 and 6000 mg/l (Table 1). These sulfate ions can penetrate through the cement matrix, leading to damage. In fully buried structures, the ingressing sulfates react with aluminate hydrates to produce ettringite and gypsum, the antagonists of chemical sulfate attack. Failure is typically marked by expansion, cracking and spalling of a concrete specimen (Marchand and Skalny, 1999; Skalny, 1992). Softening and loss of strength are also possible failure methods (Mehta, 1992; Rasheeduzzafar *et al.*, 1994). Thankfully, the process is slow and can take years to manifest itself (Monteiro and Kurtis, 2003).

Damage can also be caused by the precipitation of sulfate salts in porous structures such as concrete. This physical form of damage, however, requires some form of drying of the solution for the sulfates to crystallise in pores. Such a mechanism can be encountered in tidal zones, where a cyclic wetting and drying phenomenon can occur, and in half buried structures for example. Naturally both chemical and physical attack can occur in one single specimen (Nehdi *et al.*, 2014).

Chemical sulfate attack

Sulfate ingress

Sulfate attack requires intimate contact between sulfate anions and the cement paste of the concrete. Therefore, if sulfate attack

Chemical characteristic		XA1	XA2	XA3
SO_4^{2-}	mg/l	$\geqslant$200 and $\leqslant$600	>600 and $\leqslant$3000	>3000 and $\leqslant$6000
Carbon dioxide aggressive	mg/l	$\geqslant$15 and $\leqslant$40	>40 and $\leqslant$100	>100 up to saturation
NH^{4+}	mg/l	$\geqslant$15 and $\leqslant$30	>30 and $\leqslant$60	>60 and $\leqslant$100
Mg^{2+}	mg/l	$\geqslant$300 and $\leqslant$1000	>1000 and $\leqslant$3000	>3000 up to saturation
pH		$\leqslant$6·5 and $\geqslant$5·5	<5·5 and $\geqslant$4·5	<4·5 and $\geqslant$4·0

Table 1. Limiting value for exposure classes for chemical attack from groundwater (BS EN 206:2013, BSI, 2013)

is to be anything more than superficial, ions must be transported from the surface into the concrete bulk. Sulfate ingress is driven by a concentration gradient (diffusion), and impeded by the permeability of the sample. Consequently, it has been shown that the use of a lower water/cement ratio (w/c) will result in better resistance to external sulfate attack (Monteiro and Kurtis, 2003). Yu *et al.* (2013) measured the sulfate profile of Portland cement mortars immersed in a sodium sulfate solution and were able to identify three distinct zones

(*a*) an outer surface lacking in sulfate, owing to the absence of calcium to bind the element
(*b*) an increasing sulfate concentration to a maximum at a depth of 0·5–1 mm
(*c*) a gradual decrease in sulfate concentration to background levels over a depth of several millimetres.

Yu *et al.* observed that the penetration depth remained unvaried with sample size and concentration of the solution.

Precipitation of ettringite

The most common image of sulfate attack is associated with the precipitation of ettringite, leading to expansion and cracking. Ettringite is a calcium sulfoaluminate hydrate with a composition of $C_6AS_3H_{32}$. As such, the penetrating sulfates need to find a source of aluminium and calcium with which to react. Aluminium is distributed among unreacted material and several hydrates, including calcium-silicate-hydrate (C-S-H), hydrotalcite and, most commonly, AFm phases. The conversion of AFm to ettringite requires provision of an extra two calcium atoms ($Ca/Al_{AFt} = 6$). This may be sourced from the calcium hydroxide.

The actual conversion from monosulfate to ettringite is in fact not expansive (Hime and Mather, 1999; Skalny *et al.*, 2002). Instead, the reaction is associated with an overall loss of volume. However, the precipitation of ettringite, at the expense of monosulfate, results in a doubling in solids volume, increasing from 312·7 ml/mol to 714·9 ml/mol. The same situation applies to the precipitation of gypsum from portlandite (increasing from 33·2 ml/mol to 74·2 ml/mol) (Eglington, 1998). It is this increase, in solid volume, which is the origin of the expansion and cracking seen upon sulfate attack.

Although it would be convenient to explain concrete failure as being attributable to an increase in solids volume, it is not enough to explain degradation upon ettringite precipitation. There is no link between the amount of ettringite and/or gypsum precipitation and the extent of expansion (Kunther *et al.*, 2013a; Odler and Colan-Subauste, 1999). Lothenbach *et al.* (2010) showed that the increase in solids volume upon sulfate attack did not exceed the total capillary porosity, when modelling for changes in phase assemblage for a neat mortar exposed to either 4 g/l or 44 g/l of sodium sulfate (Figure 1). Therefore, if the expansive agents formed only in the capillary pores, then no expansion should occur. As such, ettringite must precipitate in confined spaces to cause damage.

With such attention attributed to ettringite formation, it follows that preventing its formation can assist in attempting to improve sulfate resistance. Decreasing the overall tricalcium aluminate content, which reacts with water and sulfate to form ettringite, can result in improved resistance to sulfate attack. Several studies have shown that a lower tricalcium aluminate content can lead to improved resistance (Monteiro and Kurtis, 2003; Ouyang *et al.*, 1998; Verbeck, 1967). The impact of reducing the tricalcium aluminate content is widely recognised and sulfate-resisting cements have been subsequently devised (Type V from ASTM C150/C150M-12 (ASTM, 2012) and the CEM I-SR series from BS EN 197–1:2011 (BSI, 2011)).

Precipitation of gypsum

In addition to work on ettringite precipitation, previous work has probed the role of gypsum formation and found that its precipitation also leads to expansion (Gonzalez and Irassar, 1997; Santhanam *et al.*, 2003a; Tian and Cohen, 2000). Wang (1994) even stated that gypsum formation is more damaging than the formation of ettringite. However, the aforementioned studies rely on the use of strongly concentrated, circa 5% sodium sulfate, solutions.

Gypsum precipitation is dependent on the sulfate concentration and the pH of the solution. As the pH increases, so must the sulfate content (Bellmann *et al.*, 2006). This agrees with thermodynamic investigations (Damidot and Glasser, 1993; Lothenbach *et al.*, 2010), with gypsum predicted to precipitate at higher sulfate concentrations. Some studies have seen the formation of gypsum in already formed cracks (Gollop and Taylor, 1992; Schmidt *et al.*, 2009) and as such its impact on expansion can be debated. Schmidt *et al.* (2009) stated that the role of gypsum precipitation in cement exposed to a strongly sulfate solution was to open up cracks which were already present. Planel *et al.* (2006), however, noticed the presence of gypsum in cement pastes exposed to a much lower concentration; that is, 0·015 mol/l (2·1 g/l) of sodium sulfate. This is supported by other studies (Chabrelie, 2010; El-Hachem *et al.*, 2012a).

Leaching

As sulfates ingress inwards, calcium hydroxide leaches out of the cement paste, releasing Ca^{2+} and OH^-, plus alkalis (Adenot and Buil, 1992; Kamali *et al.*, 2003, 2008; Planel *et al.*, 2006; Revertegat *et al.*, 1992; Roziere and Loukili, 2011). This is plotted in Figure 2, where the extent of leaching shows a linear relationship with the square root of time, typical of diffusion-based reactions. With the leaching of these species, the pH of the pore solution is reduced causing calcium-silicate-hydrate to decalcify; this is marked by a gradual reduction in the calcium/silicon of the phase (Adenot and Buil, 1992). The lower pH also causes ettringite to decompose to gypsum at a $pH < 10{\cdot}7$ (Gabrisova and Havlica, 1991).

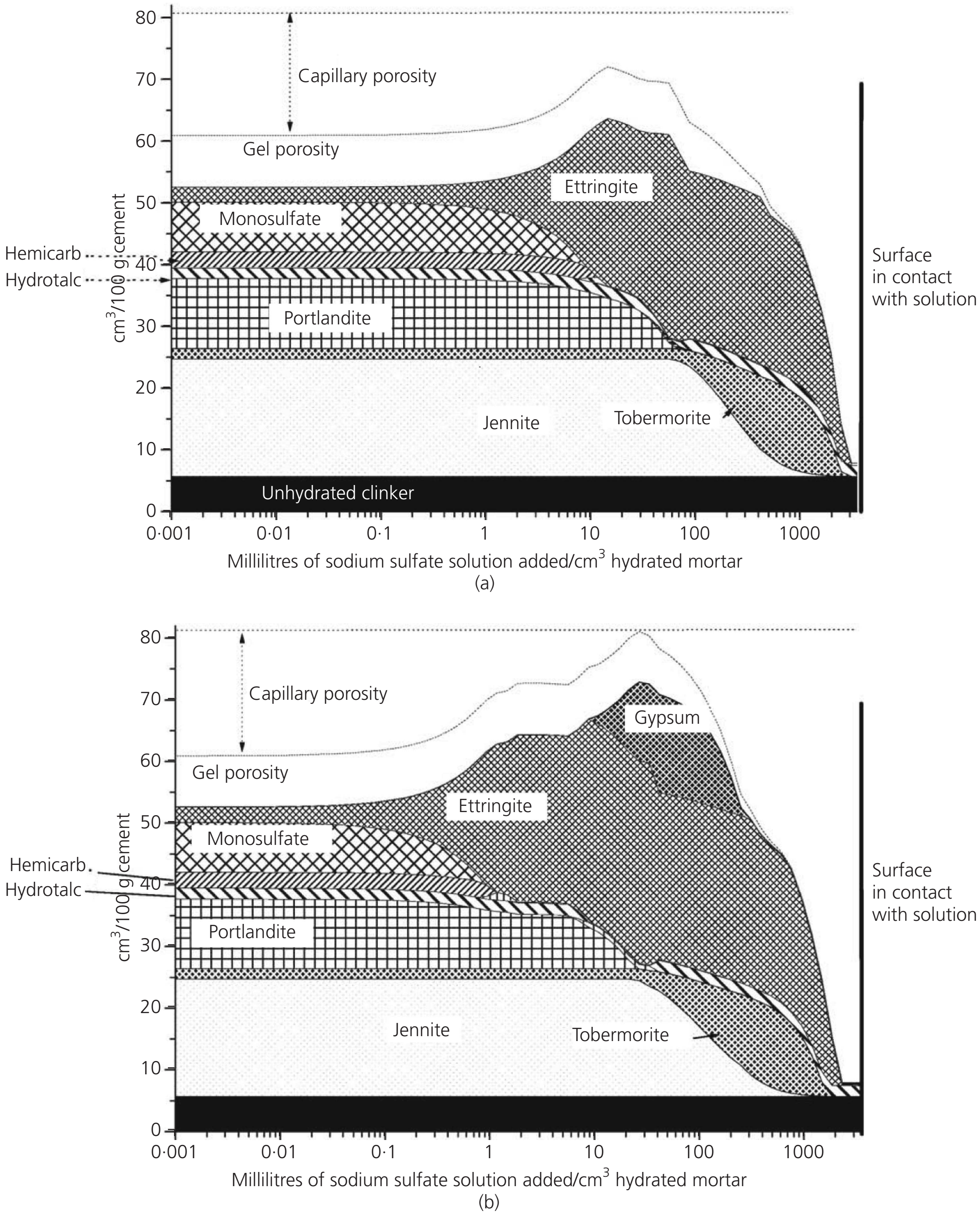

Figure 1. Phase assemblage of mortar samples immersed in (a) 4 g/l sodium sulfate and (b) 44 g/l sodium sulfate (Reprinted from Lothenbach B, Bary B, Le Bescop P, Schmidt T and Le Terrier N (2010) Sulfate ingress in Portland cement. *Cement and Concrete Research* **40**: 1211–1225; Copyright Lothenbach *et al.* (2010), with permission from Elsevier)

Leaching results in the softening and loss of strength of the cement paste as the porosity increases (Carde and Francois, 1997). The leaching kinetics are dependent on the nature of the surrounding solution. The extent of leaching is dependent on the pH (Roziere *et al.*, 2009) and temperature of the solution, the sulfate source, the w/c of the sample and the use of supplementary cementing materials (SCMs) (Kamali *et al.*, 2003, 2008). A more concentrated solution can also promote leaching. As such, leaching effects should be taken into account when evaluating sulfate attack (El-Hachem *et al.*, 2012a).

Figure 3 summarises the physicochemical changes usually

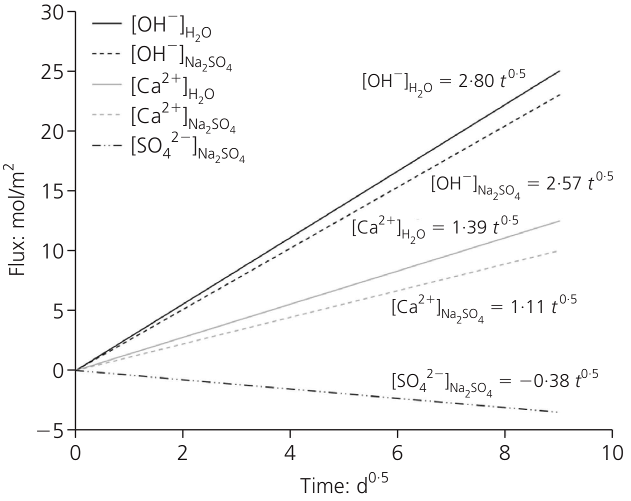

Figure 2. Kinetics of leaching of Ca^{2+} and OH^- (tested in deionised water) and ingress of SO_4^- (tested in sodium sulfate solution) (Reprinted from Planel D, Sercombe J, Le Bescop P, Adenot F and Torrenti JM (2006) Long-term performance of cement paste during combined calcium leaching-sulfate attack: kinetics and size effect. *Cement and Concrete Research* **36**: 137–143. Copyright (Planel *et al.*, 2006), with permission from Elsevier))

observed in cement when exposed to sulfates. The model assumes a sodium sulfate solution, with only the sulfate-bearing fraction reacting.

Expansion mechanism

Over the years, several theories have been put forward to explain why expansion occurs upon ettringite precipitation (Brown and Taylor, 1999). The more common ones are briefly explained below.

Swelling pressure

Mehta (1973) suggested that ettringite imbibing water could cause expansive swelling pressure, when working with sulfoaluminate cements mixed with lime and gypsum. It should be noted that in the presence of lime, ettringite takes the form of a colloidal solid; with its high specific surface area adsorbing water molecules (Mehta, 1982). Brown and Taylor (1999) stated that swelling is a typical property of gel-like materials, being flexible to withstand swelling. However, ettringite is not usually observed to form a gel and its internal structure cannot take more than 36 moles of water, making this theory unlikely to be the underlying cause of expansion owing to ettringite formation.

Topochemical growth

Another, early, theory stated that ettringite grows topochemically (Cohen, 1983; Lafuma, 1930). This theory, however, appears unlikely owing to the different crystal structures of tricalcium aluminate, AFm and ettringite. Instead, ettringite appears more likely to precipitate by a through-solution mechanism.

Crystallisation pressure

The more recent theory of crystallisation pressure (Correns, 1949; Flatt, 2002; Flatt and Scherer, 2008; Scherer, 1999, 2004) appears to be a more plausible mechanism behind expansion. The theory states that a crystal (ettringite) can precipitate from solution, supersatured with respect to the phase. The maximum pressure exerted is then given by (Kunther *et al.*, 2013a)

$$\Delta P = \frac{RT}{V_m} \ln \frac{\text{IAP}}{K_{s0}}$$

where ΔP is the pressure needed to halt crystal grown in a pore, R is molar gas constant, T is temperature (K), V_m is molar volume, IAP is ion activity product and K_{s0} is the equilibrium solubility product.

The ratio (IAP/K_{s0}) is the supersaturation ratio. The system is stable if the ratio equals 1. If greater, ettringite will precipitate; and if lower, ettringite will dissolve. It is also necessary for a crystal to grow in a confined space, opposing growth, in order to cause pressure. The stress generated in a single pore is insufficient to cause damage, and growth must occur on a larger scale.

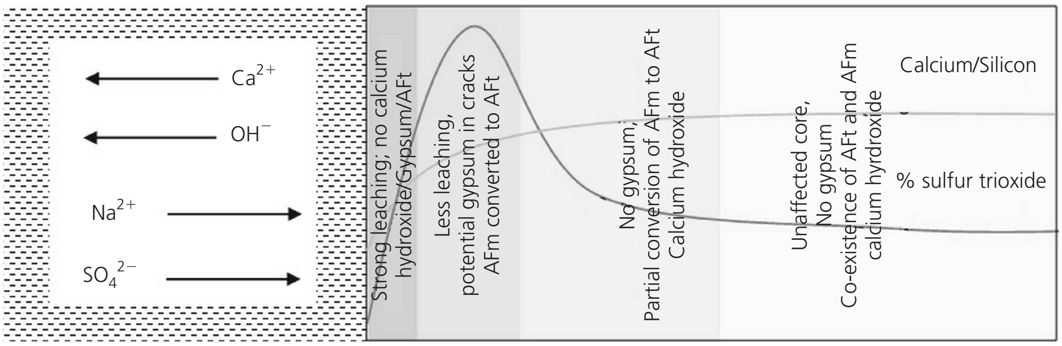

Figure 3. Schematic diagram of physicochemical changes typically observed during sulfate attack, assuming a sodium sulfate solution with only sulfates reacting

Crystallisation pressure is also dependent on pore size, humidity, pH and the existence of solid solutions (Flatt and Scherer, 2008; Scherer, 1999, 2004). The application of crystallisation pressure has recently been applied to external sulfate attack (Mullauer *et al.*, 2013; Yu *et al.*, 2013). Yu *et al.* (2013) calculated a crystallisation pressure as high as 21 MPa from a solution supersatured with respect to ettringite, exposing samples to a 30 g/l sodium sulfate solution.

Thaumasite sulfate attack

Thaumasite sulfate attack (TSA) is a form of sulfate attack differing from conventional attack in that it involves the interaction of an external source of sulfate with calcium-silicate-hydrate. Thaumasite has no binding capacity, resembling a 'white, incohesive mush' (Skalny *et al.*, 2002). As a result, in the UK, the Thaumasite Expert Group was formed and identified numerous occurrences of TSA (Thaumasite Expert Group, 2000, 2002).

During TSA, the calcium and the silica react together with sulfates and carbonates, primarily at low temperatures, as shown below

$$3Ca^{2+} + SiO_3{}^{2-} + CO_3{}^{2-} + SO_4{}^{2-} + 15H_2O \rightarrow 3CaO.SiO_2.CO_2.SO_3.15H_2O$$

The phase usually precipitates at lower temperatures (<15°C) (Blanco-Varela *et al.*, 2006; Schmidt *et al.*, 2008; Zhou *et al.*, 2006). Although some studies have seen the formation at higher temperatures (Diamond, 2003; Irassar, 2009; Sahu *et al.*, 2002). Limestone cements have been shown to be less resistant to TSA (Justnes, 2003; Ramezanianpour and Hooton, 2013). Meanwhile, Nobst and Stark (2003) showed that more thaumasite formed in tricalcium aliminate and aluminium oxide rich cements. They also pointed out that even low tricalcium aluminate cements were susceptible to thaumasite attack. This was confirmed by Blanco-Varela *et al.* (2006), who concluded that more thaumasite was formed in tricalcium-aluminate-poor cements compared to tricalcium-aluminate-rich cements, albeit with slower kinetics. In cement devoid of tricalcium aluminate, however, no thaumasite was noticed (Aguilera *et al.*, 2003). Bellmann and Stark (2008) demonstrated the role of portlandite, which worsened resistance when present. Perhaps consequently, the use of blended systems appeared to improve resistance to TSA (Bellmann and Stark, 2008; Higgins, 2003; Torii *et al.*, 1995).

Thaumasite resembles ettringite from a structural point of view (Bensted, 1999; Collepardi, 1999; Macphee and Diamond, 2003), where the alumina has been substituted by six-fold coordinated silicate ions. In fact, the presence of ettringite is considered a precursor for thaumasite formation. Thaumasite, however, is more easily stabilised at higher sulfur trioxide/aluminium oxide ratios, greater than that required for ettringite (sulfur trioxide/aluminium oxide = 3) (Macphee and Barnett, 2004; Schmidt *et al.*, 2009); and a solid solution, woodfordite, exists between the two phases (Barnett *et al.*, 2003; Damidot *et al.*, 2004; Macphee and Barnett, 2004). A study by Kohler *et al.* (2006) found a link between ettringite and thaumasite such that ettringite controls the rate of thaumasite formation.

The mechanism of thaumasite formation has been widely discussed (Bensted, 2003; Crammond, 2003). Bensted (2003) proposed two different mechanisms. First, a direct route whereby carbonates reacted with sulfates, silicates (from calcium-silicate-hydrate) and calcium in excess water. Second, by the woodfordite route, where ettringite, silicates and carbonates react together. According to Crammond (2003), thaumasite could either form topochemically from ettringite, substituting [Si] and [$SO_4{}^{-2} + H_2O$] for [Al] and [$CO_3 + SO_4{}^{2-}$], respectively, or through solution; where thaumasite will precipitate if sulfate and carbonates are present, and all the aluminium has been consumed to form ettringite.

Impact of the sulfate source

Sulfates within groundwater do not exist in isolation, but co-exist with other anions and cations. The nature of the cation has been found to play an important role in sulfate attack, and has been the subject of considerable investigation.

Calcium sulfate

Calcium sulfate is perhaps the least aggressive salt, primarily because of its lower solubility (1·46 g/l of $SO_4{}^{2-}$) (Skalny *et al.*, 2002). This makes it an unsuitable salt for use in laboratory simulations to assess sulfate resistance. Still, continued exposure to the salt in field conditions can, over time, lead to some damage (Bellmann *et al.*, 2012).

Alkali sulfates

Alkali sulfates include both potassium and sodium sulfates. Sodium sulfate is perhaps the most widely used salt for assessing sulfate attack. This may be attributed to its high solubility.

Conversely, little work is available on the use of potassium sulfate. Both Hooton and Emery (1990) and Kunther *et al.* (2013a) immersed mortar samples in potassium sulfate solutions, both finding rapid expansion. A thermodynamic (Kunther *et al.*, 2013a) study predicted that ettringite would be precipitated, plus possibly syngenite $K_2Ca(SO_4)_2.H_2O$.

An early study looked at the role of alkali sulfates in sulfate attack and drew parallels with the conditions required for ASR attack (Pettifer and Nixon, 1980), finding both sulfate attack and ASR in several structures.

Magnesium sulfate

Magnesium sulfate will initially react with calcium hydroxide, to produce magnesium hydroxide (brucite) and gypsum, according to the reaction shown below

$$\mathrm{Mg^{2+} + SO_4{}^{2-} + Ca(OH)_2 + 2H_2O \rightarrow}$$
$$\mathrm{Mg(OH)_2 + CaSO_4.2H_2O}$$

Brucite will take the form of a layer close to the surface of the sample, with a sub-layer of gypsum (Gollop and Taylor, 1992; Santhanam *et al.*, 2002) lying just beneath this. The layer of brucite can, however, offer some level of protection, reducing permeability (Santhanam *et al.*, 2003b), but sulfate can still diffuse through the brucite layer to form ettringite deeper into the sample where the pH is higher. The barrier does eventually break, accelerating the degradation mechanism.

The aggressive nature of the salt is a consequence of brucite's very low solubility. A solution saturated in brucite will have a pH of 10·5, too low to stabilise calcium-silicate-hydrate and ettringite. As a result, greater decalcification can occur. The combined action of magnesium with sulfate makes this salt particularly aggressive, especially in the absence of calcium hydroxide.

Magnesium sulfate can lead to the formation of magnesium-silicate-hydrate (M-S-H) (Al-Amoudi, 2002; Gollop and Taylor, 1992). Gollop and Taylor (1995) measured a magnesium/silicon of 1·5 for the phase, suggesting a phase similar in composition to crystalline serpentine, having a composition $M_3S_2H_2$. Bonen and Cohen (1992) meanwhile suggested a composition closer to M_2SH_x.

Mixed solutions

Most laboratory tests make use of ideal solutions, where only one cation is associated with the sulfate. In reality, several different cations may be present in sulfate-laden water sources. Kunther *et al.* (2013a, 2013b) compared the performance of mortar prisms exposed to various sulfate solutions, including a mixture of different sulfate salts. One of the two studies compared the expansion of at a CEM I mortar prism exposed to a mixed-cation solution and a dilute magnesium sulfate solution (Kunther *et al.*, 2013b); the overall sulfate content was much greater in the mixed-cation solution. Nonetheless, the extents of expansion of the two samples were comparable. The authors only speculated that the different ions somehow affected the degree of supersaturation with respect to ettringite. However, the mechanism of magnesium sulfate attack differs from that of sodium sulfate, making any comparison difficult.

Impact of supplementary cementitious materials and additives on chemical sulfate attack

The use of supplementary cementitious (pulverised fly ash (PFA), ground granulated blast furnace slag (GGBS) and silica fume) materials have often been used to suppress sulfate attack, helping to minimise both ettringite and gypsum formation, plus helping to resist thaumasite attack (Barcelo *et al.*, 2014; Higgins and Crammond, 2003; Skaropoulou *et al.*, 2013). BS EN 197-1:2011 (BSI, 2011) allows the use of slags or pozzolans, with a minimum content of 66% and 21% by weight, respectively. According to Al-Amoudi (2002) the use of blends aids sulfate resistance in three ways.

(*a*) Diluting the clinker species. Reducing tricalcium aluminate and tricalcium silicate contents results in less aluminate hydrates and portlandite to react with sulfates. SCMs are usually calcium deficient compared to cement (Bye, 2011).
(*b*) Pozzolans further reduce the portlandite content as they hydrate. Slags may also consume calcium hydroxide, but to a lesser extent. As such, less portlandite is available to form gypsum or to provide calcium to form ettringite.
(*c*) Blended systems usually exhibit a finer pore structure, reducing permeability (Bijen, 1996), and thereby improving resistance.

Fly ash

A minimum fly ash content of 20% can effectively lead to improved resistance against sulfate attack (Irassar and Batic, 1989; Mangat and El-Khatib, 1995; Torii and Kawamura, 1994; Torii *et al.*, 1995). As explained above, this is mostly attributable to the pozzolanic reaction of the fly ash consuming an already diluted portlandite content. However, the composition of the fly ash must not be ignored, and calcium-rich fly ash can prove to be poorly performing. Consequently, an R-factor was devised and defined as (Dunstan, 1980)

$$R = \frac{\%\mathrm{CaO} - 5}{\%\mathrm{Fe_2O_3}}$$

If R is less than 1·5, then a fly ash can be assumed to perform satisfactorily. Mehta (1986) argued that this was insufficient, and suggested rather that it is the nature of the aluminate hydrates present prior to sulfate exposure (ratio of ettringite to monosulfate, depending on the sulfate content and reactive alumina) which determines the suitability of a fly ash.

Silica fume

A blend of up to 15% silica fume with cement has previously been shown to provide good resistance upon exposure to sodium sulfate solutions (Lee *et al.*, 2005). This is a result of a denser microstructure provided by the hydration of the finer silica fume particles (Song *et al.*, 2010). However, such blends perform poorly when exposed to magnesium sulfate (Al-Amoudi, 2002; Bonen and Cohen, 1992; Lee *et al.*, 2005). Such blended systems are depleted with respect to portlandite, and any ingressing magnesium will subsequently react initially with calcium-silicate-hydrate to form brucite and gypsum, and ultimately magnesium-silicate-hydrate.

Ground granulated blast furnace slag

Composite systems containing slag can also help prevent sulfate attack (Gollop and Taylor, 1996a, 1996b; Higgins, 2003; Hooton and Emery, 1990; Locher, 1966; Ogawa *et al.*, 2012). The behaviour of such systems is dependent on the level of replacement and the composition of the slag. Slag cement blends typically behave adequately when slag levels are high (70%). This effect is amplified when using slags with lower aluminium oxide contents.

The use of high levels of slags to improve resistance may appear to be counterintuitive with their higher aluminium content. Aluminium released during hydration is distributed between calcium-silicate-hydrate, aluminate hydrates (AFt and AFm), and hydrotalcite, plus any remaining in unreacted slag. Only aluminium bound by the AFm is readily available to react with sulfates. Gollop and Taylor (1996a, 1996b) discussed the impact of how aluminium is distributed in such systems. Slag cements produce a calcium-silicate-hydrate phase with a lower calcium/silicon ratio, which allows it to bind more aluminium in its structure. The hydrotalcite phase also binds aluminium; how much depends on the composition of the slag (both the magnesium content of slag, plus its magnesium/aluminium ratio). Combined calcium-silicate-hydrate and hydrotalcite can actually bind much of the aluminium released, hiding it from sulfates, the impact of which is greatest in blends with high levels of slags, potentially improving resistance.

The role of a lack of aluminium availability can be seen in alkali activated systems. Komljenović *et al.* (2013) found that an alkali activated slag system outperformed a CEM II/A-S system. The better resistance of the former resulted from the fact that aluminium was bound to the calcium-silicate-hydrate and hydrotalcite, and therefore unavailable to react with sulfates.

Still, Fernandez-Altable (2009) also showed that during sulfate attack, aluminium reacts with sulfates to form secondary monosulfate prior to forming secondary ettringite, where ingressing sulfates react with aluminium from slags. This effect would explain why slag blended systems show improved resistance. He further stated that resistance of a blend is dependent on the initial amount of AFm present at low levels (40%) of slag replacement and the overall aluminium oxide content at higher levels (70%).

Impact of gypsum

A few studies have been concerned with the impact of additional gypsum, when adding more than that already present to regulate setting, on sulfate resistance (Freeman and Carrasquillo, 1995; Gollop and Taylor, 1996a; Higgins, 2003; Ogawa *et al.*, 2012). Gollop and Taylor (1996a) studied a series of slag-containing blends, one of which contained 65% slag with added gypsum. This last mix showed a much better resistance when compared to blends with 69% slag without gypsum; the sulfate slag blend performed as well as a slag blend containing 92% slag without added sulfates. Similarly, better resistance of fly ash blends containing added gypsum has been seen when samples were exposed to a 10% sodium sulfate solution (Freeman and Carrasquillo, 1995). The work found an optimum sulfate content, beyond which sample resistance worsened due to increased susceptibly to volume instability. The use of additional gypsum favours ettringite precipitation over AFm phases at early ages, before the occurrence of sulfate attack (Whittaker *et al.*, 2014). With more of the original aluminium now bound, less is available to subsequently react with sulfates.

Impact of limestone addition

While often considered to be an inert filler, limestone is actually partially reactive. Its effect is seen in the distribution of the aluminate hydrates; carbonate-AFm phases being preferentially formed over monosulfate, the expelled sulfate then allowing for the stabilisation of AFt (Matschei *et al.*, 2007). Ogawa *et al.* (2012) and Higgins and Crammond (2003) reported improved sulfate resistance upon low levels of limestone addition, although the former cautioned that the resistance is limited as the carbonate AFm, which initially formed with the added carbonated, may very well convert to ettringite.

BS EN 197-1:2011 (BSI, 2011) allows for the replacement of cement with limestone, up to 35% by weight. Irassar (2009) recently reviewed the use of limestone cements in the presence of sulfates. He concluded that low levels of replacement (<10%) would have no detrimental effects, but resistance would worsen at higher levels. This was attributed to the increase of the effective w/c of the system, increasing porosity and favouring penetration of the sulfates (Schmidt *et al.*, 2009). Limestone can also promote the thaumasite form of sulfate attack (Irassar, 2009).

Physical sulfate attack

Mechanism

Sulfate attack may manifest itself physically when dissolved salts diffuse through the concrete and precipitate in pores, causing damage (Haynes *et al.*, 2008; Rodriguez-Navarro *et al.*, 2000; Scherer, 2004; Thaulow and Sahu, 2004). A particularly pernicious salt is sodium sulfate (Flatt, 2002; Rodriguez-Navarro *et al.*, 2000; Tsui *et al.*, 2003). Two crystalline sodium sulfate salts exist; thenardite ($NaSO_4$) and mirabilite ($NaSO_4.10H_2O$). A solution of thenardite is supersaturated with respect to mirabilite at temperatures below 32°C and humidities above 75%; the precipitation of mirabilite can then cause damage (Flatt, 2002; McMahon *et al.*, 1992; Steiger and Asmussen, 2008). Rodriguez-Navarro *et al.* (2000) noted that at relative humidities above 40%, mirabilite would form first from a supersaturated solution of sodium sulfate, which would subsequently convert to thenardite. Below 40% relative humidity (RH), thenardite would be precipitated directly. Several damage mechanisms have been proposed and have been summarised previously (Thaulow and Sahu, 2004), putting forward the idea of crystallisation pressure (Correns, 1949; Scherer, 2004).

Cyclic wetting and drying cycles can favour such damage (Chabrelie, 2010; Haynes *et al.*, 2008; Sahmaran, 2007). The salt precipitates in the drying cycle, where the humidity is allowed to drop. It is usually during the wetting cycle that damage is observed (Flatt, 2002), where in the case of sodium sulfate, existing thenardite dissolves and the solution is supersaturated again with respect to mirabilite.

Scherer (2004) partially submerged porous stone in a sodium sulfate solution which penetrated the sample by capillary action. As the solution percolated upwards, efflorescence took place on the side of the sample and subflorescence occurred within the samples, where the rate of evaporation matched that of the water rise (Figure 4). Parallels may be drawn between this study and similar situations arising in concrete. Concrete samples subjected to semi-immersion have been tested in the past, in both field and laboratory conditions (Chabrelie, 2010; Irassar *et al.*, 1996; Nehdi *et al.*, 2014). The immersed portions will be subjected to chemical sulfate attack, whereas the exposed regions will expect to fail due to salt crystallisation. As such, both actions may have to be considered.

Effect of supplementary cementitious materials on physical sulfate attack

Although the use of SCMs may aid, delay or prevent sulfate attack, the same cannot be said in the event of physical sulfate attack (Chabrelie, 2010; Irassar *et al.*, 1996; Nehdi *et al.*, 2014). Nehdi *et al.* (2014) investigated partially immersed concrete samples. While the immersed parts suffered from conventional chemical sulfate attack, mirabilite crystallised above the water level, causing further damage. In concretes containing pozzolans (fly ash, metakaolin and silica fume), damage from physical attack was greater in comparison to samples free from pozzolans, owing to an increased pores of smaller diameter. This increased capillary suction and the surface area for drying. This agrees with a similar study carried out by Irassar *et al.* (1996).

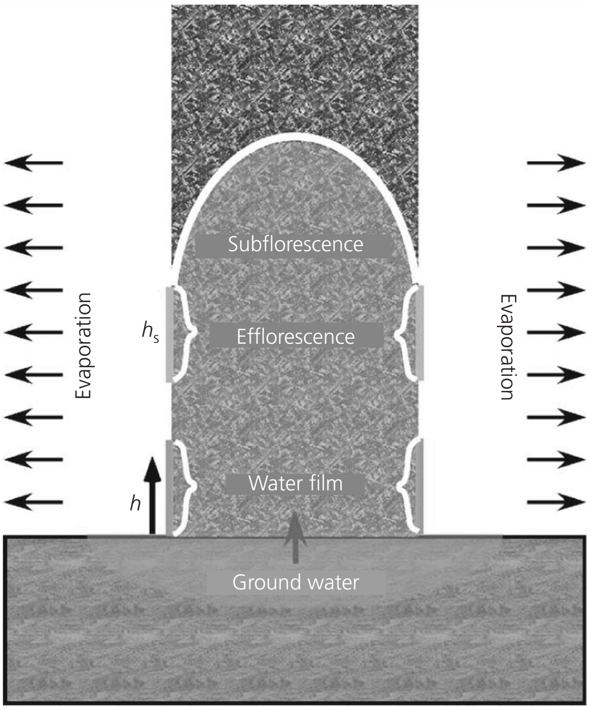

Figure 4. Schematic diagram of capillary rise through a porous material in contact with groundwater (Reprinted from Scherer GW (2004) Stress from crystallisation of salt. *Cement and Concrete Research* **34**: 1613–1624. Copyright (Scherer, 2004), with permission from Elsevier))

Sulfate attack in field conditions

Several studies have been concerned with the performance of concrete exposed to sulfates in field conditions (Bellmann *et al.*, 2012; Chabrelie, 2010; Drimalas, 2007; Harrison, 1992; Irassar *et al.*, 1996; Mehta, 1992; Novak, 1989; Stroh *et al.*, 2014). In such conditions, sulfates present in water sources (groundwater, river water, etc.) or from the oxidation of sulfide minerals (pyrite, marcasite, pyrrhotite), can penetrate the cement matrix. Key issues with field studies are that concentrations are typically lower than in laboratory simulations, and there is a mix of different sulfate species.

It is also important to know how the structures interact with the sulfate source. This is seen when comparing two separate studies carried out on samples either partially immersed (Irassar *et al.*, 1996) or fully immersed (Stroh *et al.*, 2014) in sulfate-laden soils, for 5 and 19 years, respectively. The same materials were used for both studies, exposed in the same, sulfate-rich, soil (approx. 1% SO_4^{2-}). The impact of admixtures (slags, fly ash and a natural pozzolan) was also studied in these two studies. In fully buried samples, the blended systems were reported to perform the best. However, in half buried samples, the half exposed to the atmosphere showed greater damage in the blended system.

Bellmann *et al.* (2012) assessed the performance of 20 structures across Thuringia, Germany. Some of the structures contained supplementary cementitious materials, and assessing the impact of cement type was made difficult because of the wide range of exposure conditions. The structures were grouped depending on the exposure conditions, reflecting the variability in which concrete structures can be exposed to sulfates. Most of the structures behaved adequately, with only six of the structures being seriously damaged. Often structures showed the formation of thaumasite, and the more damaged structures were in contact with sulfide-rich rock or soil, where low pH can worsen resistance, owing to an acid attack of the concrete. Structures, however, showed limited damage when exposed to rivers and groundwater, where the sulfate concentrations were lowest.

Mehta (1992) carried out a review of sulfate attack on concrete structures in field conditions. He concluded that cracking and failure is rarely ever attributed to sulfate attack alone, and that weathering and increased permeability of the concrete through micro cracking must also occur. He further stated that structures fail by decohesion and loss of strength owing to the decomposition of cement hydrates.

Experimental considerations

Standards

Owing to the multitude of factors influencing sulfate attack in the field, laboratory tests must be simplifications of such real-life scenarios. The most common standard used to assess sulfate resistance is the American standard ASTM C1012-13M (ASTM, 2013), testing the resistance of samples exposed to chemical sulfate attack. The standard relies on using mortar prisms of a specified mix design and of a given minimum compressive strength. These prisms are fully immersed in a 5% sodium sulfate solution, although the solution can be substituted for another salt (magnesium sulfate). The solution, which by volume is four times that of the sample, is renewed at specified intervals. The extent of sulfate attack is then determined by measuring only linear expansion of the prisms. There is no equivalent European standard, although BS EN 206:2013 (BSI, 2013) does recognise several exposure classes and specifies several attributes of the concrete to be used accordingly.

The American standard, however, does have its limitations. First, soon after immersion, the samples will start leaching Ca^{2+} and OH^-, resulting in the decomposition of calcium hydroxide and calcium-silicate-hydrate, quickly raising the pH of the surrounding solution to approximately 12·5.

Second, the concentration of the solution greatly exceeds what is expected to be found in natural conditions. The implications of this were previously debated by Bellmann *et al.* (2006). A highly concentrated solution would favour the formation of gypsum, typically not observed in field conditions, along with ettringite precipitation. Furthermore, the solution used is only associated with one cation when more may be present in field water sources.

A further limitation is that performance is assessed solely on the extent of expansion. Ion exchange with the bathing solution results in leaching of cement hydrates, leading to softening, decohesion and ultimately degradation of the sample. The loss of strength, elastic modulus and mass change are also indicative of damage, but not probed by the standard.

The Rilem report TC 25-PEM (Rilem, 1980) made recommendations on how to assess the performance of stones exposed to sulfate resistance subjected to wetting/drying cycles and partial immersion. The experimental procedures described in these studies may very well be adapted to concrete samples to test for other field set-ups, although some issues remain without adaption. For instance, the drying cycle (section V.1a and V.1b) (Rilem, 1980) relies on drying samples at 105°C, which could result in dehydration of calcium-silicate-hydrate and ettringite.

Effect of sample preparation

In the assessment of the chemical impact of sulfate attack on cementitious binders, several factors must be considered. Careful planning may help to better simulate field conditions. Some of these are detailed below. Fewer studies have been carried out on physical sulfate attack, for which no standard is readily available.

Size

Larger samples show better resistance (El-Hachem *et al.*, 2012a; Ferraris *et al.*, 2005; Planel *et al.*, 2006; Yu *et al.*, 2013) to expansion. El-Hachem *et al.* (2012a) showed that the onset of expansion was delayed when increasing mortar prisms from $10 \times 10 \times 100\ mm^3$ to $70 \times 70 \times 280\ mm^3$ in size. Yu *et al.* (2013) discussed the occurrence of expansive forces, which occur when sulfates penetrate that are restrained by the core. Larger samples will require a greater section subject to expansion to overcome the restraining effect of the core.

Curing conditions

As sulfate attack relies on the transport of aggressive ions into the cement matrix, resistance is dependent on how the sample is prepared. Mangat and El-Khatib (1992) compared the resistance of air-cured and water-cured samples, and found the former to be more resistant; this is attributed to the formation of a carbonation layer, opposing sulfate ingress. Fernandez-Altable (2009) further showed that expansion of core samples, cut from larger samples, expanded faster that non-cut samples; the act of cutting removed the carbonation layer, plus surface laitance.

Water/cement ratio

The w/c ratio also plays a vital role in sulfate resistance, with its reduction increasing sulfate resistance (Al-Akhras, 2006; El-Hachem *et al.*, 2012b; Monteiro and Kurtis, 2003; Sahmaran *et al.*, 2007). Specimens made with higher w/c result in an increase in porosity and permeability (Khatri and Sirivivatnanon, 1997), favouring sulfate ingress and worsening resistance. Monteiro and Kurtis (2003) suggested a ‘safe domain’, setting the w/c as low as 0·45, below which structures will perform adequately.

Interfacial transition zone

The presence of the interfacial transition zone (ITZ) can also affect sulfate resistance. This zone is characterised by having a higher porosity (Bourdette *et al.*, 1995) than the bulk paste. The zone is also usually richer in portlandite (Ollivier *et al.*, 1995). Bonakdar *et al.* (2012) varied the sand/calcium ratio of specimens (by using pastes and mortars), an increase in which led to greater expansion of prisms. This was attributed to the higher diffusivity around the ITZ. El-Hachem *et al.* (2012a) found that the ITZ was rich in calcium and sulfate but poor in aluminium after exposing samples to a sulfate solution, indicating the presence of gypsum. This was previously observed by Bonen and Sarkar (1993).

Effect of exposure conditions

Effect of sulfate concentration

The use of a highly concentrated solution has already been debated by Bellmann *et al.* (2006). The use of highly concentrated solutions (El-Hachem *et al.*, 2012a; Mullauer *et al.*, 2013; Schmidt *et al.*, 2009; Yu *et al.*, 2013) usually accelerate attack, although Yu *et al.* (2013) noticed that the penetration depth of sulfate in mortar samples is independent of the sulfate concentration. Highly concentrated sulfate solutions, however, will favour the formation of gypsum (Bellmann *et al.*, 2006; Lothenbach *et al.*, 2010).

Effect of solution renewal

Fernandez-Altable (2009) compared the effect of solution renewal on expansion, exposing samples to renewed and non-renewed sodium sulfate solutions. Expansion was delayed in the former case. He attributed this effect to a reduction of the pH hindering ettringite growth. Lothenbach *et al.* (2010) modelled the effect of leaching, which was greatest if the solution continuously flowed.

Effect of the pH

To simulate field conditions better, some experimental set-ups allow for pH control (Cao *et al.*, 1997; Chabrelie, 2010; El-Hachem *et al.*, 2012b; Planel *et al.*, 2006; Roziere and Loukili, 2011; Wang, 1994) Cao *et al.* (1997) found a reduction in expansion when reducing the pH of the bathing solution in a neat system, which they attributed to greater calcium-silicate-hydrate decalcification. Brown (1981) on the other hand found a faster onset of expansion when reducing the pH of the solution. Chabrelie (2010) carried out testing at constant pH and found that the leaching of the solution was prevented when the solution was not renewed. Still, expansion was accelerated. Slag blended systems (Cao *et al.*, 1997) appeared to be greatly affected by the pH, which worsened resistance as the pH decreased in blends whose slag content was lower than 60%. Contrarily, PFA and silica fume blended systems performed admirably regardless of the pH.

Conclusions/remarks

Sulfate attack is a widely researched degradation mechanism, and yet it is still to be fully understood. External sulfate attack defines a series of interactions which occur within concrete, and can be classified as either being chemical or physical.

In the event of chemical sulfate attack, macroscopic investigations are marked by expansion, ultimately cracking and/or spalling. Expansion is perhaps the most common form of assessing sulfate attack, as decreed by the standard ASTM C1012-13M (ASTM, 2013). Loss of strength, dynamic modulus and a change in mass is also indicative of damage. Softening and decohesion may also occur. All of these observations are the result of internal changes of the microstructure. Sulfates react with aluminate hydrates to produce ettringite, precipitating from a supersatured solution; its growth exerts pressure in small pores, causing damage. The role of gypsum is still debated, with it being stabilised when highly concentrated solutions are used. Some studies, however, have noticed the presence of gypsum when weaker solutions are used.

Typical investigations have relied on laboratory studies to assess resistance. Typically these are accelerated, by using strongly concentrated solutions. The approach, however, often does not necessarily reflect field conditions. This is recognised, and more recent studies change exposure conditions (pH, renewal, concentration) so as to better mimic field conditions.

Recently, attention has been given to physical sulfate attack. Physical sulfate attack does not entail any reaction with the hydrates. It is simply the recrystallisation of sulfate salts in pores as the solution is allowed to dry. Drying can happen if exposure is cyclic or when specimens are semi-immersed. In the latter case, dissolved salts rise through the sample by capillary action, before recrystallising where the humidity drops. There is still, however, no standardised test for this sort of exposure.

The extent of damage is dependent on the nature of the mix. In the case of chemical sulfate attack, the use of supplementary cementitious materials, combined with low w/c, will result in improved performance. In the event of physical sulfate attack, the use of SMCs, however, can worsen damage as greater capillary action can arise from a refined pore structure.

REFERENCES

Adenot F and Buil M (1992) Modelling of the corrosion of the cement paste by deionized water. *Cement and Concrete Research* **22(2–3)**: 489–496.

Aguilera J, Martinez-Ramirez S, Pajares-Colomo I and Blanco-Valera MT (2003) Formation of thaumasite in carbonated mortars. *Cement and Concrete Composites* **25(8)**: 991–996.

Al-Akhras NM (2006) Durability of metakaolin concrete to sulfate attack. *Cement and Concrete Research* **36(9)**: 1727–1734.

Al-Amoudi OS (2002) Attack on plain and blended cements exposed to aggressive sulfate environments. *Cement and Concrete Composites* **24(3–4)**: 305–316.

ASTM (2012) ASTM C150/C150M-12: Standard specification for Portland cement. ASTM International, West Conshohocken, PA, USA.

ASTM (2013) ASTM C1012/C1012M-13: Standard test method for length change of hydraulic-cement mortars exposed to a sulfate solution. ASTM International, West Conshohocken, PA, USA.

Barcelo L, Gartner E, Barbarulo R *et al.* (2014) A modified ASTM C1012 procedure for quantifying blended cements containing limestone and SCMS for use in sulfate-rich environments. *Cement and Concrete Research* **63**: 75–88.

Barnett SJ, Macphee DE and Crammond NJ (2003) Extent of immiscibility in the ettringite–thaumasite system. *Cement and Concrete Composites* **25(8)**: 851–855.

Bellmann F and Stark J (2008) The role of calcium hydroxide in the formation of thaumasite. *Cement and Concrete Research* **38(10)**: 1154–1161.

Bellmann F, Moser B and Stark J (2006) Influence of sulfate solutions concentration on the formation of gypsum in sulfate resistance test specimen. *Cement and Concrete Research* **36(2)**: 358–363.

Bellmann F, Erfurt W and Ludwig H-M (2012) Field performance of concrete exposed to sulphate and low pH conditions from natural and industrial sources. *Cement and Concrete Composites* **34(1)**: 86–93.

Bensted J (1999) Thaumasite – background and nature in deterioration of cements. Mortars and concretes. *Cement and Concrete Composites* **21(2)**: 117–121.

Bensted J (2003) Thaumasite – direct, woodfordite and other possible formation routes. *Cement and Concrete Composites* **25(8)**: 873–877.

Bijen J (1996) Benefits of slag and fly ash. *Construction of Building Materials* **10(5)**: 309–314.

Blanco-Varela MT, Aguilera J and Martinez-Ramirez S (2006) Effect of cement C_3A content, temperature and storage medium on thaumasite formation in carbonated mortars. *Cement and Concrete Research* **36(4)**: 707–715.

Bonakdar A, Mobasher B and Chawla N (2012) Diffusivity and micro-hardness of blended cement materials exposed to external sulfate attack. *Cement and Concrete Composites* **34(1)**: 76–85.

Bonen D and Cohen MD (1992) Magnesium sulfate attack on Portland cement paste II. *Chemical and Mineralogical Analyses* **I(22)**: 707–718.

Bonen D and Sarkar SL (1993) Replacement of portlandite by gypsum in the interfacial zone related to crystallization pressure. *Ceramic Transaction, Proceedings of 95th Annual Meeting, Cement-Based Materials: Present, Future, and Environmental Aspects*. ACI, Westerville, OH, USA, pp. 49–60.

Bourdette B, Ringot E and Olliver JP (1995) Modelling of the transition zone porosity. *Cement and Concrete Research* **25(4)**: 741–751.

Brown PW (1981) An evaluation of the sulfate resistance of cements in a controlled environment. *Cement and Concrete Research* **11(5–6)**: 719–727.

Brown PW and Taylor HF (1999) The role of ettringite in external sulfate attack. In *Materials Science of Concrete: Sulfate Attack Mechanism, Special Volume* (Marchand J and Skalny J (eds)). The American Ceramic Society, Westerville, OH, USA, pp. 73–98.

BSI (2011) BS EN 197-1:2011: Cement part I: Composition, specifications and conformity for common cements. BSI, London, UK.

BSI (2013) BS EN 206:2013: Concrete – specification, performance, production and conformity. BSI, London, UK.

Bye G (2011) *Portland Cement*, 3rd edn. ICE Publishing, London, UK.

Cao HT, Bucea L, Ray A and Yozghatlian S (1997) The effect of cement composition and pH of environment of sulfate resistance of Portland and blended cements. *Cement and Concrete Composites* **19(2)**: 161–171.

Carde C and Francois R (1997) Effect of the leaching of calcium hydroxide from cement paste on mechanical and physical properties. *Cement and Concrete Research* **27(4)**: 539–550.

Chabrelie A (2010) *Mechanisms of Degradation of Concrete by External Sulfate Ions Under Laboratory and Field Conditions*. PhD thesis, EPFL, Lausanne, Switzerland.

Cohen MD (1983) Modeling of expansive cements. *Cement and Concrete Research* **13(4)**: 519–528.

Collepardi M (1999) Thaumasite formation and deterioration in historic buildings. *Cement and Concrete Composites* **21(2)**: 147–154.

Collepardi M (2003) A state-of-the-art review on delayed ettringite attack on concrete. *Cement and Concrete Composites* **25(4–5)**: 401–407.

Correns CW (1949) Growth and dissolution of crystals under linear pressure. *Discussions of the Faraday Society* **5**: 267–271.

Crammond NJ (2003) The thaumasite form of sulfate attack in the UK. *Cement and Concrete Composites* **25(8)**: 809–818.

Damidot D and Glasser FP (1993) Thermodynamic investigation of the CaO-Al_2O_3-$CaSO_4$-H_2O system at 25°C and the influence of Na_2O_3. *Cement and Concrete Research* **23(1)**: 221–238.

Damidot D, Barnett SJ, Glasser FP and Macphee DE (2004) Investigation of the CAO-AL_2O_3-SIO_2-$CASO_4$-$CACO_3$-H_2O system at 25°C by thermodynamic calculation. *Advances in Cement Research* **16(2)**: 69–76, http://dx.doi.org/10.1680/adcr.2004.16.2.69.

Diamond S (2003) Thaumasite in Orange County, Southern California: an inquiry into the effect of low temperature. *Cement and Concrete Composites* **25(8)**: 1161–1164.

Drimalas T (2007) *Laboratory and Field Evaluations of External Sulfate Attack*. PhD thesis, University of Texas, Austin, USA.

Dunstan ER (1980) A possible method for identifying fly ashes that will improve the sulfate resistance of concrete. *Cement, Concrete, and Aggregates* **2(1)**: 20–30.

Eglington M (1998) Resistance of concrete to destructive agencies. In *Lea's Chemistry of Cement,* 4th edn. Butterworth-Heinemann, London, UK, pp. 299–342.

El-Hachem R, Roziere E, Grondin F and Loukili A (2012a) Multi-criteria analysis of the mechanism of degradation of Portland cement based mortars exposed to external sulphate attack. *Cement and Concrete Research* **42(10)**: 1327–1335.

El-Hachem R, Roziere E, Grondin F and Loukili A (2012b) New procedure to investigate external sulphate attack on cementitious materials. *Cement and Concrete Composites* **34(3)**: 357–364.

Fernandez-Altable V (2009) Availability of Al_2O_3 in slag blended cements: sulphate attack implications. *Proceedings of the Final Conference of the NANOCEM Marie Curie Research Training Network, Villars-sur-Ollon, Switzerland*.

Ferraris C, Stutzman P, Peltz M and Winpigler J (2005) Developing a more rapid test to assess sulfate resistance of hydraulic cements. *Journal of Research of the National Institute of Standards and Technology* **110(5)**: 529–540.

Flatt RJ (2002) Salt damage in porous materials: how high supersaturations are generated. *Journal of Crystal Growth* **242(3–4)**: 435–454.

Flatt RJ and Scherer GW (2008) Thermodynamics of crystallization stresses in DEF. *Cement and Concrete Research* **38(3)**: 325–336.

Freeman RB and Carrasquillo RL (1995) Adjustement in gypsum content for the production of sulfate-resistant blended cements containing high-calcium fly ash. *ACI Materials Journal* **92(4)**: 411–418.

Gabrisova A and Havlica J (1991) Stability of calcium sulphoaluminate hydrates in water solutions with various pH values. *Cement and Concrete Research* **21(6)**: 1023–1027.

Gollop RS and Taylor HF (1992) Microstructural and microanalytical studies of sulfate attack I – ordinary Portland cement paste. *Cement and Concrete Research* **22(6)**: 1027–1038.

Gollop RS and Taylor HF (1995) Microstructural and microanalytical studies of sulfate attack III. Sulfate-resisting Portland cement: reactions with sodium and magnesium sulfate ions. *Cement and Concrete Research* **25(7)**: 1581–1590.

Gollop RS and Taylor HF (1996a) Microstructural and microanalytical studies of sulfate attack, V, comparison of different slag blends. *Cement and Concrete Research* **27(7)**: 1029–1044.

Gollop RS and Taylor HF (1996b) Microstructural and microanalytical studies of sulfate attack IV – reactions of a slag cement paste with sodium and magnesium sulfate solutions. *Cement and Concrete Research* **26(7)**: 1013–1028.

Gonzalez MA and Irassar EF (1997) Ettringite formation in low C_3A Portland cement exposed to sodium sulfate solution. *Cement and Concrete Research* **27(7)**: 1061–1072.

Harrison WH (1992) *Sulphate Resistance of Buried Concrete: Third Report on a Long Term Investigation at Northwick Park and on Similar Concretes in Sulphate Solutions*. Building Research Establishment, Garston, UK, Publication BR 164.

Haynes H, O'Neill R, Neff M and Mehta PK (2008) Salt weathering distress on concrete exposed to sodium sulfate environment. *ACI Materials Journal* **105(1)**: 35–43.

Higgins DD (2003) Increased sulfate resistance of GGBS concrete in the presence of carbonate. *Cement and Concrete Composites* **25(8)**: 913–919.

Higgins DD and Crammond NJ (2003) Resistance of concrete containing GGBS to the thaumasite form of sulfate attack. *Cement and Concrete Composites* **25(8)**: 921–929.

Hime WG and Mather B (1999) 'Sulfate attack', or is it? *Cement and Concrete Research* **29(5)**: 789–791.

Hooton RD and Emery JJ (1990) Sulfate resistance of a Canadian slag cement. *ACI Materials Journal* **87(6)**: 547–555.

Irassar EF (2009) Sulfate attack on cementitious materials containing limestone filler – a review. *Cement and Concrete Research* **39(3)**: 241–254.

Irassar EF, Di Maio A and Batic OR (1996) Sulfate attack on concrete with mineral admixtures. *Cement and Concrete Research* **26(1)**: 113–123.

Irassar F and Batic O (1989) Effects of low calcium fly ash on sulfate resistance of OPC cement. *Cement and Concrete Research* **19(2)**: 194–202.

Justnes J (2003) Thaumasite formed by sulfate attack on mortar with limestone filler. *Cement and Concrete Composites* **25(8)**: 955–959.

Kamali S, Gerard B and Moranville M (2003) Modelling the leaching kinetics of cement-based materials – influence of materials and environment. *Cement and Concrete Composites* **25(4–5)**: 451–458.

Kamali S, Moranville M and Leclercq S (2008) Material and environmental parameters effects on the leaching of cement pastes: experiments and modelling. *Cement and Concrete Research* **38(4)**: 575–585.

Khatri RP and Sirivivatnanon V (1997) Role of permeability in in sulphate attack. *Cement and Concrete Research* **27(4)**: 1179–1189.

Kohler S, Heinz D and Urbonas L (2006) Effect of ettringite on thaumasite formation. *Cement and Concrete Research* **36(4)**: 697–706.

Komljenović M, Baščarević Z, Marjanović N and Nikolić V (2013) External sulfate attack on alkali-activated slag. *Construction and Building Materials* **49**: 31–39.

Kunther W, Lothenbach B and Scrivener KL (2013a) On the relevance of volume increase for the length changes in mortar bars in sulfate solution. *Cement and Concrete Research* **46**: 23–29.

Kunther W, Lothenbach B and Scrivener KL (2013b) Deterioration of mortar bars immersed in magnesium containing sulfate solutions. *Materials and Structures* **46(12)**: 2003–2011.

Lafuma H (1930) Theorie de l'expansion des liants hydrauliques. *La Revue des Materiaux de Construction et de Travaux Publics*. pp. 441–444, Part 1, 243, 1929; part 2, 244, 4–8.

Lee ST, Moon HY and Swamy RN (2005) Sulfate attack and role of silica fume in resisting strength loss. *Cement and Concrete Composites* **27(1)**: 65–76.

Locher FW (1966) The problem of the sulfate resistance of slag cements. *Zement-Kalk-Gibs* **9**: 395–401.

Lothenbach B, Bary B, Le Bescop P, Schmidt T and Leterrier N (2010) Sulfate ingress in Portland cement. *Cement and Concrete Research* **40(8)**: 1211–1225.

Macphee DE and Barnett SJ (2004) Solution properties of solids in the ettringite-thaumasite solid solution series. *Cement and Concrete Research* **34(9)**: 1591–1598.

Macphee D and Diamond S (2003) Thaumasite in cementitious materials. *Cement and Concrete Composites* **25(8)**: 805–807.

Mangat PS and El-Khatib JM (1992) Influence of initial curing on sulphate resistance of blended cement concrete. *Cement and Concrete Research* **22(6)**: 1089–1100.

Mangat PS and El-Khatib JM (1995) Influence of fly ash, silica fume and slag on sulfate resistance of concrete. *ACI Materials Journal* **92(5)**: 542–552.

Marchand J and Skalny JP (1999) *Materials Science of Concrete: Sulfate Attack Mechanisms. Special Volume*. American Ceramic Society, OH, USA.

Matschei T, Lothenbach B and Glasser FP (2007) The AFm phase in Portland cement. *Cement and Concrete Research* **37(2)**: 118–130.

McMahon D, Sandberg P, Folliard K and Mehta P (1992) Deterioration mechanisms of sodium sulfate. *Proceedings of the 7th International Congress on Deterioration and Conservation of Stone, Lisbon, Portugal*, pp. 705–714.

Mehta PK (1973) Mechanism of expansion associated with ettringite formation. *Cement and Concrete Research* **3(1)**: 1–6.

Mehta PK (1982) Expansion of ettringite by water adsorption. *Cement and Concrete Research* **12(1)**: 121–122.

Mehta PK (1986) Effect of fly ash composition on sulfate resistance of cement. *Proceedings of the American Concrete Institute* **83(6)**: 994–1000.

Mehta PK (1992) Sulfate attack on concrete – a critical review. In *Materials Science of Concrete* (Skalny SJ and Skalny J (eds)). American Ceramic Society, Westerville, OH, USA, vol. III, pp. 105–130.

Monteiro PJ and Kurtis KE (2003) Time to failure for concrete exposed to severe sulfate attack. *Cement and Concrete Research* **33(7)**: 987–993.

Mullauer W, Beddoe RE and Heinz D (2013) Sulfate attack expansion mechanisms. *Cement and Concrete Research* **52**: 208–215.

Nehdi ML, Suleiman AR and Soliman AM (2014) Investigation of concrete exposed to dual sulphate attack. *Cement and Concrete Research* **64**: 42–53.

Nobst P and Stark J (2003) Investigations on the influence of cement type on thaumasite formation. *Cement and Concrete Composites* **25(8)**: 899–906.

Novak GA (1989) Efflorescent mineral assemblages associated with cracked and degraded residential concrete foundations in southern California. *Cement and Concrete Research* **19(1)**: 1–6.

Odler I and Colan-Subauste J (1999) Investigations on cement expansion associated with ettringite formation. *Cement and Concrete Research* **29(5)**: 731–735.

Ogawa S, Nozaki T, Yamada K, Hirao H and Hooton RD (2012) Improvement on sulfate resistance of blended cement with high alumina slag. *Cement and Concrete Research* **42(2)**: 244–251.

Ollivier JP, Maso JC and Bourdette B (1995) Interfacial transition zone in concrete. *Advances in Cement Based Materials* **2(1)**: 30–38.

Ouyang C, Nanni A and Chang WF (1998) Internal and external sources of sulfate ions in Portland cement mortar: two types of chemical attack. *Cement and Concrete Research* **18(5)**: 699–709.

Pettifer K and Nixon PJ (1980) Alkali metal sulphate – a factor common to both alkali aggregate reaction and sulphate attack on concrete. *Cement and Concrete Research* **10(2)**: 173–181.

Planel D, Sercombe J, Le Bescop P, Adenot F and Torrenti JM (2006) Long-term performance of cement paste during combined calcium leaching-sulfate attack: kinetics and size effect. *Cement and Concrete Research* **36(1)**: 137–143.

Ramezanianpour AM and Hooton RD (2013) Thaumasite sulfate attack in Portland and Portland-limestone cement mortars exposed to sulfate solution. *Construction and Building Materials* **40**: 162–173.

Rasheeduzzafar, Al-Amoudi OS, Abduljauwad SN and Maslehuddin M (1994) Magnesium-sodium sulfate attack in plain and blended cements. *Journal of Materials in Civil Engineering* **6(2)**: 201–222.

Revertegat E, Richet C and Gegout P (1992) Effect of pH on the durability of cement pastes. *Cement and Concrete Research* **22(2–3)**: 259–272.

Rilem (1980) Rilem TC 25-PEM: Recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods. *Materials and Structures* **13(75)**: 175–253.

Rodriguez-Navarro C, Doehne E and Sebastian E (2000) How does sodium crystallize? Implications for the decay and testing of building materials. *Cement and Concrete Research* **30(10)**: 1527–1534.

Roziere E and Loukili A (2011) Performance-based assessment of concrete resistance to leaching. *Cement and Concrete Composites* **33(4)**: 451–456.

Roziere E, Loukili A, El-Hachem R and Grondin F (2009) Durability of concrete exposed to leaching and external sulphate attacks. *Cement and Concrete Research* **39(12)**: 1188–1198.

Sahmaran M (2007) Sodium sulphate attack on blended cements under different exposure conditions. *Advances in Cement Research* **19(2)**: 47–56, http://dx.doi.org/10.1680/adcr.2007.19.2.47.

Sahmaran M, Kasap O, Duru K and Yaman IO (2007) Effects of mix composition and water-cement ratio on the sulfate resistance of blended cements. *Cement and Concrete Composites* **29(3)**: 159–167.

Sahu S, Badger S and Thaulow N (2002) Evidence of thaumasite formation in southern California concrete. *Cement and Concrete Composites* **24(3–4)**: 379–384.

Santhanam M, Cohen MD and Olek J (2002) Mechanism of sulfate attack: a fresh look part I: summary of experimental results. *Cement and Concrete Research* **32(6)**: 915–921.

Santhanam M, Cohen MD and Olek J (2003a) Effects of gypsum formation on the performance of cement mortars during external sulfate attack. *Cement and Concrete Research* **33(3)**: 325–332.

Santhanam M, Cohen MD and Olek J (2003b) Mechanism of sulfate attack: a fresh look part II: proposed mechanisms. *Cement and Concrete Research* **33(3)**: 341–346.

Scherer GW (1999) Crystallisation in pores. *Cement and Concrete Research* **29(8)**: 1347–1358.

Scherer GW (2004) Stress from crystallisation of salt. *Cement and Concrete Research* **34(9)**: 1613–1624.

Schmidt T, Lothenbach B, Romer M *et al.* (2008) A thermodynamic and experimental study of the conditions of thaumasite formation. *Cement and Concrete Research* **38(3)**: 337–349.

Schmidt T, Lothenbach B, Romer M, Neuenschwander J and Scrivener K (2009) Physical and microstructural aspects of sulfate attack on ordinary and limestone blended Portland cements. *Cement and Concrete Research* **39(12)**: 1111–1121.

Skalny J (1992) *Materials Science of Concrete*. American Ceramic Society, OH, USA, vol. III.

Skalny J, Marchand J and Odler I (2002) *Sulphate Attack on Concrete*. Spon, London, UK.

Skaropoulou A, Sotiriadis K, Kakali G and Tsivilis S (2013) Use of mineral admixtures to improve the resistance of limestone cement concrete against thaumasite form of sulfate attack. *Cement and Concrete Composites* **37**: 267–275.

Song HW, Pack SW, Nam SH, Jang JC and Saraswathy V (2010) Estimation of the permeability of silica fume cement concrete. *Construction and Building Materials* **24(3)**: 315–321.

Steiger M and Asmussen S (2008) Crystallization of sodium sulfate phases in porous materials: the phase diagram $NASO_4$-H_2O and the generation of stresses. *Geochimica et Cosmochimica Acta* **72(17)**: 4291–4306.

Stroh J, Schlegel MC, Irassar E, Meng B and Emmerling F (2014) Applying high resolution SyXRD analysis on sulfate attacked concrete field samples. *Cement and Concrete Research* **66**: 19–26.

Taylor HF, Famy C and Scrivener KL (2001) Delayed ettringite formation. *Cement and Concrete Research* **31(5)**: 683–693.

Thaulow N and Sahu S (2004) Mechanism of concrete deterioration due to salt crystallization. *Materials Characterisation* **53(2–4)**: 123–127.

Thaumasite Expert Group (2000) *Thaumasite Expert Group Report One-Year Review.* Prepared by Professor L A Clark and BRE. See http://www.planningportal.gov.uk/uploads/odpm/4000000009287.pdf (accessed 08/2014).

Thaumasite Expert Group (2002) *Thaumasite Expert Group Report: Review After Three Years Experience*. Prepared by Professor L A Clark and BRE. See http://www.planningportal.gov.uk/uploads/odpm/4000000009288.pdf (accessed 08/2014).

Tian B and Cohen MD (2000) Does gypsum formation during sulphate attack on concrete lead to expansion. *Cement and Concrete Research* **30(1)**: 117–123.

Torii K and Kawamura M (1994) Effects of fly ash and silica fume on the resistance of mortar to sulfuric acid and sulfate attack. *Cement and Concrete Research* **24(2)**: 361–370.

Torii K, Taniguchi K and Kawamura M (1995) Sulfate resistance of high fly ash content of concrete. *Cement and Concrete Research* **25(4)**: 759–768.

Tsui N, Flatt RJ and Scherer GW (2003) Crystallization damage by sodium sulfate. *Journal of Cultural Heritage* **4(2)**: 109–115.

Verbeck GJ (1967) *Field and Laboratory Studies of the Sulphate Resistance of Concrete*. Portland Cement Association, Skokie, IL, USA, Research Bulletin 227.

Wang JG (1994) Sulfate attack on hardened cement paste. *Cement and Concrete Research* **24(4)**: 735–742.

Whittaker M, Zajac M, Ben Haha M, Bullerjahn F and Black L (2014) The role of the alumina content of slag, plus the presence of additional sulfate on the hydration and microstructure of Portland cement-slag blends. *Cement and Concrete Research* **66**: 91–101.

Yu C, Sun W and Scrivener K (2013) Mechanism of expansion of mortars exposed in sodium sulphate solutions. *Cement and Concrete Research* **43**: 105–111.

Zhou Q, Hill J, Byars EA *et al.* (2006) The role of pH in thaumasite sulfate attack. *Cement and Concrete Research* **36(1)**: 160–170.

WHAT DO YOU THINK?

To discuss this paper, please submit up to 500 words to the editor at journals@ice.org.uk. Your contribution will be forwarded to the author(s) for a reply and, if considered appropriate by the editorial panel, will be published as a discussion in a future issue of the journal.