DEVELOPMENT OF TEST METHODS TO ADDRESS THE VARIOUS MECHANISMS OF SULFATE ATTACK

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Abstract

Existing test methods in standards were typically designed to only evaluate the resistance of the aluminate phases in cements or cementitious materials to sulfate attack. Even then, tests often only assess expansion after immersion in concentrated solutions of sodium sulfate at temperatures of 20 to 23°C, which does not mimic resistance to other sulfate types, concentrations and temperatures. For example, at low temperatures the thaumasite form of sulfate attack on the calcium silicate matrix may occur, and at early-age temperatures in excess of 70°C, delayed ettringite formation may occur, without exposure to an external source of sulfates. While it is known that design of concrete to provide resistance to sulfate penetration is vital, because of the lack of standard tests for measurement of sulfate transport rates, as an indirect method, standards typically place maximum limits on water to cementing materials ratios. In this contribution the different forms of sulfate attack are discussed as well as the role of tests and models for prediction of resistance.

1. INTRODUCTION

Development of test methods to determine resistance of concretes to sulfate exposures is complicated by the fact that there are different forms and aggressivenesses of sulfate attack which vary as a function of concentration, the cation(s) associated with the sulfate ions, presence of other ions (eg. seawater), temperature, and boundary conditions of the structural concrete element. Damage can occur due to chemical attack on the aluminate phases in the cementing materials, due to chemical attack on the calcium-silicate matrix, due to acidic dissolution of the matrix, or due to physical attack due to sulfate salt crystallization in pores near surfaces subjected to drying. This complexity, combined with the slowness of many forms of sulfate attack, conspires against adoption of a single performance test method, and in some cases requires adoption of prescriptive approaches (such as w/cm limits, or limits on allowable cement types). For many decades, many national building codes and specifications have adopted a combination of performance and prescriptive options to address sulfate attack, and in general this has greatly reduced the potential for failures due to sulfate attack. While these measures were thought to provide protection against sulfate deterioration, since the 1990’s, a number of sulfate-related problems have been identified which
may not be adequately addressed in current standards. These include delayed ettringite formation, sulfate salt crystallization, and thaumasite sulfate attack.

One question facing the RILEM committee on Performance in Aggressive Environments (TC-PAE) is whether new materials-science-based tests be developed that provide improved predictions of performance?

It is important to understand the different mechanisms involved in order to develop appropriate test methods. Unfortunately, engineers and materials scientists have spent significant time arguing about whether, for example, physical salt attack is really part of sulfate attack. From a holistic point of view, if damage occurs due to exposure to sulfate ions, then it needs to be addressed regardless. The real question to a designer using Building codes is: can damage due to sulfate exposure be prevented by taking appropriate measures in materials selection, mix proportioning, or in the construction practices used? Owners of a building or structure are not concerned about the specific mechanisms involved, they just want a structure that will be durable over its intended service life, in the environment to which it is exposed. However, it is up to materials scientists and engineers to develop the appropriate tests and guidance in standards and building codes so that premature deterioration is prevented.

2. DIFFERENT TYPES OF SULFATE ATTACK

2.1 External Attack

2.1.1 Calcium aluminate reactions with sulfate

In this form of sulfate attack, solutions containing dissolved sulfates intrude concrete pore structures. If transport is limited by diffusion, these sulfates will move through concrete porosity relatively slowly. If an evaporative front is present, transport is assisted by advective flow which is capable of substantially accelerating the rate of sulfate ingress. As sulfate solutions enter the pore structure of concrete, they may then react with sources of calcium to form gypsum and with sources of alumina to eventually form ettringite. Depending on the source of alumina, ettringite (Aft) formation may occur directly or its formation may be preceded by that of monosulfate. The latter is more likely in concrete containing supplementary cementing materials in that they supply supplementary sources of alumina. In spite of an increased potential for ettringite formation, however, blended cement concretes, if produced at low water-to-cementitious materials ratios, are generally regarded as more resistant to sulfate attack because their resistances to fluid penetration are increased by the pozzolanic reaction.

The mechanistic path of this type of sulfate attack is reasonably well understood with respect to the formation of those compounds which cause damage. It is also recognized that different types of damage may occur. A typical measure of sulfate attack in laboratory mortar samples is the extent of expansion, as is the case with the ASTM C1012 test. However, sulfate attack of concrete may result in significant microstructural damage leading to the formation of microcracks without significant expansion. In this instance the concrete softens rather than undergoing significant bulk expansion. Other forms of microstructural damage depend on the cation associated with the sulfate anion. Sodium and magnesium sulfate cause Ca(OH)$_2$ dissolution, as calcium is required for the formation
of ettringite and gypsum. Magnesium ions may also attack the calcium silicate hydrate binder forming weak magnesium silicate hydrates and reaction with Ca(OH)$_2$ can form brucite (Mg(OH)$_2$).

Also, the formation of gypsum (calcium sulfate dihydrate, CaSO$_4$·2H$_2$O) inside pores can lead to softening and loss of concrete strength [1, 2]. The reaction of penetrating sodium or potassium sulfates with Ca(OH)$_2$ can result in gypsum formation. Ettringite is a normal product of cement hydration, so its identification in a cement-based building material does not automatically indicate that a problem has occurred or, if it has, that ettringite was the cause.

**Test Methods:** The history of development of the ASTM C452 and C1012 test methods was detailed by Hooton [3]. The first standard performance test for evaluating cements was ASTM C452 developed by Lerch [4], in which calcium sulfate is added to the mortar bar mixtures to attain 7.0% SO$_3$ content by mass of cement. This accelerates the test by eliminating the time for sulfate ingress, and assesses the resistance due to the aluminate phases in the cement. The mortar bars are stored in water from 1 to 14 days at 23°C and the expansion is measured. The ASTM C 150 expansion limit for SRPC (Type V) is 0.040% while in CSA A3001, it is 0.035% (Type HS) and 0.045% for moderate sulfate resisting (Type MS) cement.

It is still specified as an optional test for assessing the sulfate resistance of Portland cements but it was found not to be suitable for evaluation of blended cements and cementitious combinations containing supplementary cementing materials, as these systems rely on reduced permeability and reduced calcium hydroxide contents to provide resistance, and this requires hydration prior to sulfate exposure.

This led to the development of ASTM C1012 where mortar bars (w/cm = 0.485) are cured until a strength of 20 MPa is achieved, then they are exposed to 50 g/L Na$_2$SO$_4$ solution at 23°C and expansion is measured. This test method had been adopted for blended cements (ASTM C595, C1157 and CSA A3001) and for evaluating mixtures of portland cement with supplementary cementing materials (ASTM C989, C1240 and CSA A3001). The expansion test limits that have evolved [5, 6] are 0.05% at 6 months for high sulfate resistance (this can be superseded by meeting a limit of 0.10% at 12 months). For moderate sulfate resistance, the limit is 0.10% at 6 months. The ACI C201.2R guide to durability has adopted similar limits to qualify sulfate-resistant cementitious combinations for moderate and severe exposures, but also has included a very-severe exposure class where a limit of 0.10% at 18 months is required and these limits were adopted in the 2008 version of the ACI 318 building code (see Table 2).

One of the industry concerns with C1012 is the length of time required to obtain results. However, it is difficult to avoid this since sulfates must diffuse inwards to react with aluminate compounds before any expansion can occur. During development of this test, the original strength of 25 MPa before sulfate exposure was reduced to 20 MPa in order to shorten the test. In hindsight, this was counter-productive in terms of balancing the concept of allowing these blended materials to react with respect to the saving of only a few days in a six month test. As well, the test is not necessarily directly relevant to other types of sulfate salts than sodium sulfate. For example, magnesium sulfate typically results in softening and cracking of the bars without as much expansion. Therefore, visual indications of damage need to be recorded as well as expansion if other sulfate salts are substituted in this test. The original test allowed for a mixture of sodium and
magnesium sulfates but it was found that this caused problems in some cases, so sodium sulfate was adopted as the standard solution.

The pH of the solutions in the C1012 test are not controlled, but solutions are changed at every set of length change measurement: 1, 2, 3, 4, 8, 13, and 15 weeks, followed by 4, 6, 9, 12, 15, and 18 months. In interlaboratory testing, it was found that the pH of the Na2SO4 storage solutions rapidly rose to 12.8-13.0 whereas the sodium-magnesium sulfate mixture only resulted in pH of about 10. Brown [7] and Clifton et al [8] have advocated pH controlled tests; this may not model the situation of stagnant sulfates in contact with concrete foundations but it would better model flowing water situations, as in pipes.

It should be noted that the ASTM C1012 test was developed to show the susceptibility (or resistance) of a cementitious system to attack by external sulfate solutions. It was not intended to model all or any field conditions for concrete or to evaluate the impact of concrete quality. In the European Standard EN197-1, there is currently no test method for evaluating the sulfate resistance of a Portland or blended cement, due to lack of agreement on a common test method, in spite of several European countries previously having had test methods. As a result, in 2006 the CEN committee drafted an amendment A2 to EN197-1: 2000 to simply prescriptively allow a family of seven types of cement for use in sulfate resistant applications (not yet adopted). These types include three CEM I cements with either 0, 3, or 5% Bogue C3A in the clinker, as well as slag cements CEM III/B (66-80% slag), CEM III/C (81-95% slag), and pozzolan cements CEM IV/A (20-35% pozzolan), CEM IV/B (36-55% pozzolan).

Accelerated tests on cement pastes have also been developed to evaluate the sulfate resistance of cementitious materials. Mehta and Gjorv [9] cast 12.5 mm cubes and subjected them to both a saturated calcium sulfate solution and a 4% sodium sulfate solution for 28 days after being cured at 50°C for 7 days. The loss of compressive strength was measured. This test method was never adopted in standards. Reproducibility of strength tests on such small specimens was one reason. More recently, Ferraris et al [10, 11] proposed casting 10x10x40 mm paste prisms and subjecting them to 5% sodium sulfate solution after an initial curing period, and measuring expansion. This test is being considered by ASTM subcommittee C01.29 and an interlaboratory test is planned to compare results to those obtained in the C1012 test.

**Effect of Various Cations:** It is recognised that the cations associated with sulfate salts will affect the form of deterioration. It is not intended to review these effects in detail here, as detailed reviews are available [12], but generally sodium sulfate penetrates and reacts with soluble calcium ions (releasing sodium hydroxide and raising pH) as well as the hydrated calcium aluminate phases of cement to form expansive ettringite (including causing any monosulfate present to revert to ettringite). This typically manifests as expansion and cracking. Calcium sulfate is similar except that its solubility is much lower and while damaging, it is generally thought to occur more slowly, although its solubility rises rapidly in the presence of other cations such as sodium, potassium or magnesium. Magnesium sulfate will not elevate the pH as does sodium sulfate. As well, once inside the pores of concrete, in the presence of alkaline pore solutions, its solubility will rise. It will react with calcium hydroxide to form calcium sulfate and brucite, which is in itself expansive, but is also very insoluble. Magnesium can also exchange for calcium in the C-S-H, weakening the matrix as it penetrates, in addition to the sulfate ions reacting to form ettringite. Therefore, mortar bars stored in
magnesium sulfate typically exhibit softening and somewhat lower rates of expansion. A recent thesis on the effects of these different types of sulfates on concrete both subject to immersion and subject to wetting and drying has been completed by Drimalis [13] but papers from this work have not yet been published.

The ASTM C1012 test, as does the German Wittekindt [14] flat mortar prism test, normally uses exposure to sodium sulfate solutions, but it allows other sulfate solutions to be used. The ASTM C452 test uses admixed calcium sulfate to determine sulfate resistance of Portland cements.

2.1.2 Thaumasite

Thaumasite was first identified as occurring in deteriorating concrete in 1965 by Erlin and Stark [15], then much later by Bickley et al. [16], and has been extensively investigated by Crammond [17] and the Thaumasite Expert Group [18] in the UK. Ettringite and thaumasite are frequently found together in deteriorating concrete. Thaumasite can potentially form in the absence of external sulfate due to carbonation, which can decompose both ettringite (releasing sulfates) and the C-S-H binder (releasing hydrous silica), but it is not typical. External sulfate, or an inadvertent, gross excess of internal sulfate contribute to thaumasite sulfate attack and are almost exclusively associated with its formation. Similarly, if a source of readily soluble CaCO₃ is present within the concrete, thaumasite formation may occur. Thus, thaumasite may form as a consequence of sulfate ingress, of carbonation, or both. While originally thought to occur only in concretes exposed to cool temperatures, thaumasite formation has also been observed in concrete placed in temperate climates [17]. Thaumasite preferentially forms under the cold, wet, alkaline conditions typically experienced by buried concrete structures. The occurrence of thaumasite in deteriorated building materials has been identified in a number of countries worldwide including UK, USA, Canada, South Africa, France, Germany, Norway, Denmark, Switzerland, Italy and Slovenia.

The use of sulfate resisting concrete does not prevent the formation of thaumasite, because it is the calcium silicate hydrates (C-S-H), not the aluminate phases, are attacked by external sulfates. The replacement of C-S-H by thaumasite results in the softening of the cement paste matrix into a white, mushy non-cohesive mass. It can be seen from the formula for thaumasite that carbonate ions are an additional necessary ingredient. It has been suggested that calcium bicarbonate rather than calcium carbonate ions is the source of carbonate for thaumasite [19].

It is generally accepted that the formation of thaumasite (CaSiO₃·CaCO₃·CaSO₄·15H₂O) can follow two routes at temperatures below 15°C [20]. One is a direct formation from the reaction of sulphates, carbonates, silica (from C-S-H) and excess water in the presence of Ca²⁺ ions. Typical reactants in this relatively slow reaction include gypsum, calcite and C-S-H (1):

\[
\begin{align*}
C_2S_2H_3 + 2CaSO_4·2H_2O + 2CaCO_3 + 24H_2O & \rightarrow 2CaSiO_3·CaSO_4·CaCO_3·15H_2O + Ca(OH)_2
\end{align*}
\]

The other possible thaumasite formation route involves the reaction between ettringite, silica (from C-S-H), and carbonates, in the presence of Ca²⁺ ions and water. Typical reactants in this reaction are calcite and C-S-H [20] (2):

\[
\begin{align*}
C_3S_2H_3 + 2CaSO_4·2H_2O + 2CaCO_3 + 24H_2O & \rightarrow 2CaSiO_3·CaSO_4·CaCO_3·15H_2O + Ca(OH)_2
\end{align*}
\]
\[
C_3A \cdot 3CaSO_4 \cdot 32H_2O + C_3S_2H_3 + 2CaCO_3 + 4H_2O \rightarrow 2CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O + \]
\[
2CaSO_4 \cdot 2H_2O + 2Al(OH)_3 + 4 Ca(OH)_2
\]

This reaction essentially involves slow substitution of alumina by silica in ettringite [21]. This process significantly speeds up once thaumasite starts to form. Sometimes, a solid solution of ettringite and thaumasite, called woodfordite, is formed as well [20]. Due to the similar appearance of thaumasite and ettringite crystal structures, it is possible that in the past TSA was sometimes misidentified as a conventional sulphate attack.

A positive identification of thaumasite in a cement-based building material does not automatically indicate that a problem has occurred or, if it has, that thaumasite was the cause. There are two distinct ways in which thaumasite can precipitate as a reaction product within concretes and mortars [18] and the following characteristics must be taken into account during diagnosis:

The thaumasite form of sulfate attack (TSA) is visually very distinctive. It is characterised by significant damage to the cement paste matrix of the concrete/mortar. The main feature of TSA is that the hardened cement paste becomes partially or totally replaced by thaumasite. As thaumasite does not possess any binding ability, the affected cement paste is ultimately transformed into an non-cohesive mass (mush) loosely holding the aggregate particles together. Other distinguishing features include sub-parallel cracks filled with thaumasite and white haloes of thaumasite occurring around aggregate particles. TSA causes gradual softening of the matrix of a buried concrete, starting from the concrete/ground interface and progressing inwards. It can sometimes be accompanied by expansive disruption.

Thaumasite, like ettringite, can precipitate in voids and cracks without necessarily causing any disruption to the host concrete or mortar. This has been termed thaumasite formation (TF) and it can be found in concretes/mortars showing no obvious visual signs of sulfate attack. TF can also be found in concretes already damaged by other deterioration mechanisms, such as ettringite-based sulfate attack [22, 23] or alkali silica reaction [24, 25]. Although the presence of TF is more often than not innocuous, it can be a precursor to TSA, thereby indicating a potential future problem.

The following factors are all required for TSA to occur in cementitious-based building materials:

- TSA is typically associated with ingress of external sulfates. The carbonate ions needed to fuel TSA can either be derived from particles of limestone used as aggregate or cement ingredient (although 5% limestone additions to cement are not considered to be a risk [26] within the concrete or mortar itself, or can be supplied as carbonate or bicarbonate ions dissolved in the sulfate-bearing external water source. Smaller limestone particles are more reactive and it is possible that dolomitic limestone (CaMg(CO₃)₂) is more susceptible to TSA than calcitic (CaCO₃) limestones, but this is still not certain. Thaumasite preferentially forms under cold temperatures below 15°C, typical of the ground temperatures at foundation depth. Thaumasite can form at temperatures of up to 25°C, but the rate is much slower [18, 27].

**Possible Test Methods:** Currently there are no standards specifically related to its prevention. However, the papers that have been published on thaumasite, typically have tended to use mortar bar expansions or mortar cube strengths where the specimens have been stored at 5 – 10°C and monitored for change over time [28]. This writer has approached this by casting two sets of ASTM C1012 mortar bars which are immersed in sodium sulfate solution as per the standard, but with one
set of bars stored at 5 °C. While results are incomplete, it is anticipated that this approach could be used to simultaneously assess the resistance of different cementitious systems to both the ettringite and thaumasite forms of sulfate attack.

2.1.3 Sulfate Salt Crystallization

Damage due to precipitation of sulfate salts in concrete pores near drying faces can occur in tunnels, culverts, slabs on grade or in foundations subject to wetting/drying cycles or a simple evaporative front. The sulfates then precipitate as salts as the water evaporates near the drying surface [29]. These salts can build up in pores and undergo phase changes due to changes in temperature and relative humidity, resulting in expansive pressures. A common reversible transformation is that between thenardite (NaSO$_4$) and mirabilite (NaSO$_4$.10H$_2$O), which if occurring in the capillary pores, can cause progressive surface damage.

Many of the early studies in North America addressed physical sulfate attack from salt crystallization, with out acknowledging this directly. In the western part of Canada and the US, problems of premature deterioration of concrete in contact with the ground were observed in the early 20$^{th}$ century. These soils contained extremely high sulfate contents and were often called ‘alkaline soils’ in the literature. This led to several research projects both on the roles of cement composition and concrete mixture proportions.

From the 1920’s, even before the chemical reactions were understood, it was found that regardless of cement C$_3$A content, having low w/cm and low unit water contents of concrete mixtures were essential to obtaining resistance to the actions of sulfate soils. Wilson and Cleve [30] at the Portland Cement Association (PCA) conducted two field sites starting in 1921 in Montrose, Colorado and at Medicine Lake, South Dakota. Over 2000 cylinders, 250 x 600mm, were semi-immersed in sulfate soils, while the air would have been at low relative humidity. After 7 years exposure, they reported that concretes with w/c of 0.45 or less were relatively undamaged, while those with higher w/c suffered significant damage, as shown in Figure 1. The deterioration almost certainly included evaporative transport and sulfate salt crystallization.

The PCA later carried out a series of cyclic sodium sulfate immersion and evaporation tests on 150 x 150 x 900mm beams in Sacramento, California. It was found that both w/c and cement type influenced the results [29, 31]. While it was concluded that most of the damage occurred in the evaporative zone due to sulfate salt crystallization, little petrographic work was undertaken.

Several large laboratory studies were carried out at the US Bureau of Reclamation (USBR) for over 40 years. Concrete cylinders, 75 x 150 mm, are either immersed in 2.1% sodium sulfate solution or exposed to alternate wetting (in that solution) and drying cycles. An expansion of 0.5% or a loss of 40% in dynamic modulus of elasticity is considered failure. After 40 years exposure of cements with a range of C$_3$A and w/c, it was found that all the mixtures with w/c of 0.45 or less did not fail, regardless of C$_3$A content, as shown in Figure 2 taken from a summary of the USBR work published by Monteiro and Kurtis [31]. Some mixtures did not fail with w/c as high as 0.53, but others in that w/c range (0.45 to 0.53) were damaged.
Both the ACI and CSA Building Code limits on concrete quality for sulfate exposures have evolved from the work performed by the U.S. Bureau of Reclamation [33]. Both the ACI 318 and CSA A23.1 concrete codes limit the cement types and the maximum water to cementitious materials ratio (w/cm) based on the severity of the sulfate exposure. These limits are detailed in Table 2. The w/cm limits are used to obtain relatively impermeable concretes which have a discontinuous capillary pore structure, thus limiting sulfate ingress. This is regarded as the first line of defence for the concrete, with the type of cement a being secondary issue.

With regard to evaporative transport of sulfates, that results in sulfate salt crystallization damage, such as can occur with slabs on grade, culverts, or tunnel liners in low RH environments, there appears to be a consensus that this can also be minimized by provision of a low w/cm concrete with a discontinuous capillary pore structure [34]. Some have argued that the form of attack in these cases is physical, due to sulfate salt crystallization and related hydration/dehydration reactions (similar to what occurs in the ASTM C88 sulfate soundness test for aggregates) but there is almost certain that if sulfates are carried up through the pores of concrete, that various forms of chemical
sulfate attack will also occur, even if the manifestations of damage are slower. As well, the destructive phase changes associated with salt crystallization are indeed chemical, since the phase changes involve alternate dissolution and precipitation (e.g. mirabilite, Na₂SO₄·10H₂O, and thenardite, Na₂SO₄) resulting from changes in temperature and humidity (Figure 3).

![Figure 2: Time to failure as a function of w/c for cements of various C₃A contents [32]](image)

According to Scherer, during wetting and drying cycles, it is the crystallization pressure from formation of mirabilite during wetting that does most of the damage [35]. Since obtaining a low w/cm concrete is the solution to evaporative transport and subsequent salt crystallization, the argument seems a moot point and the maximum w/cm limits in the concrete standards provide protection in these situations. The destructive nature of sulphate crystallization was known in the 1920’s, as noted by Swenson and MacKenzie [36] who wrote, “Of special significance, then as now, was the finding that a concentration of soil or soil-water alkalis (i.e. sulfates) was not always a measure of the degree of deterioration to be expected, but that capillary action and subsequent evaporation were major factors.”
Test Methods: Where there is still a need for a performance test method is to evaluate concretes with different permeabilities or resistances to diffusion rather than by prescribing maximum w/cm limits. A semi-immersion test was developed by Ferraris et al [10] where either 100 x 200 mm concrete cylinders or cores or 50 x 100 mm mortar cylinders were immersed to half of their height in sodium sulfate solution with a layer of paraffin oil to prevent evaporation from the solutions. The top of the cylinders were exposed to three different conditions in air at 23 °C at either 30 and 80% rh, or 80% rh at 40 °C to obtain different possibilities of thenardite or mirabilite crystallization, as per Figure 3. Spalling was observed in the air-exposed portions of the cylinders under all 3 conditions, but the fastest deterioration occurred for the 23 °C-30% rh condition where thenardite formation would be favoured along with precipitation of supersaturated solution of mirabilite. In addition to visual observations of damage, diameters were measured at pre-determined locations with time. It was recommended that test temperatures be kept below 32 °C to maximize the rate of deterioration in agreement with Flatt [38].

2.1.4 Acid Attack involving Sulfates
The C-S-H matrix of Portland cement concrete is soluble in strong acids. It is not intended to cover this type of exposure, but the reader is referred to the work of DeBelie [39, 40, 41] for a review of aggressive acid attack and methods to evaluate concrete resistance.

2.2 Internal Sulfate Attack
2.2.1 Over-sulfated cements
Test methods: While ASTM C150 sulfate levels allowed in cements were increased several times from 1941 to 1971 [42] as cement compositions and finenesses changed to allow better
optimization of sulfate contents, more recently it was decided to leave the SO$_3$ limits alone, but allow them to be exceeded provided that it could be demonstrated that the optimum SO$_3$ content was above the stated limit (typically using the ASTM C563 optimum sulfate test). In this case a 14-day mortar bar expansion test (ASTM C1038, which had been previously adopted in Canadian CSA cement standards) was also required to be performed to show that the level of SO$_3$ in the cement would not result in adverse expansions from internal sulfate attack. This performance test appears to have been satisfactory when a 14-day expansion limit of 0.020% was specified. This test and expansion limit has been extended to blended cements and combinations of cementitious materials in the CSA A3001 specifications.

2.2.2 DEF

The term delayed ettringite formation (DEF) was first used to describe a form of deterioration in heat-cured precast concrete railway ties [43]. It was postulated that the normal early formation of ettringite was prevented due to the very high curing temperatures used, and that when exposed to moisture in service, deleterious amounts of ettringite formed resulting in expansion and cracking of the concrete. Since then, DEF has been implicated as a cause of deterioration in numerous other cases, mostly involving precast concrete elements that have been subjected to intentional heat curing during the production process or unintentional high temperature exposures at early ages. These problems have resulted in restrictions being placed on the curing process, including limits on pre-set times, heating and cooling rates, and the maximum allowable curing temperature (eg. in Germany and in the Canadian CSA A23.4 standard for precast concrete). German experience with these curing limits is that these and similar practices in Europe have been successful in eliminating damage due to DEF [12, 44, 45].

Possible test methods: As an alternative to placing limitations on curing practices, many different methods for assessing the potential for DEF problems have been proposed, but given the lack of clear field cases where DEF is the sole form of damage, assessing their reliability is difficult. Various chemical indicators of Portland cements, such as C$_3$A, SO$_3$, alkali contents, and fineness have been proposed [46] but none have shown to relate to mortar or concrete expansions, outside of the set of specimens used to develop them. Based on a large experimental study performed for the PCA (Hooton, unpublished), the most reliable approach, appears to be a performance-based test proposed by Kelham [47], using expansion of mortar bars that have been exposed to elevated temperature curing cycles. As clearly shown by Famy et al [48], leaching of alkalies from the bars (or removal alkalies from pore solution by ASR reactions) is an important issue and will accelerate DEF expansions. Therefore, casting of ASTM C1038 mortar bars (which have the same mortar composition as ASTM C1012 bars) can be cast, the molds sealed in a container over water, then exposed to elevated temperatures of at least 70°C, and monitored for expansion while subsequently stored in water (to leach alkalies). While an expansion limit of 0.10% is typically used for mortar bar tests, the question is what exposure time is adequate? The data of Ramlochan et al [49, 50], indicate that a one-year exposure period may be required if bars are stored in lime-saturated water, but Taylor et al [51] showed that 6 months appears to be adequate if bars are stored in plain water. As well, the beneficial effects of alumina-bearing pozzolans or slag additions can be assessed using this type of test [49, 50].
2.3 Defining the Exposure

Most specifications set the minimum cement type and concrete quality required based on the severity of the sulfate exposure. In the US and Canada, there are three exposure classes defined by either the concentration of dissolved sulfate ions in groundwater or by soluble sulfate ions in soils. These exposure classes are simplistic as they do not differentiate sulfate exposures by the type of sulfate or pH. These are shown in Table 1 (note that Class S0 means no special precautions are needed). In the UK a more complex set of seven exposure classes [52] based on sulfate concentration, presence of magnesium ions, pH is used as well as whether it is a Brownfield or natural soil. EN206-1-2000 has three exposure classes: XA1, XA2, and XA3. Based on the exposure class, CSA and ACI (Table 2) place limits on maximum w/cm and either restrict cement types or cementitious materials can be approved based on being within ASTM C1012 mortar bar expansion test limits. The EN206-1 standard limits cement types (for XA2 and XA3) and prescribes minimum cement contents as well as maximum w/c requirements for concrete.

The test method used to determine sulfates can affect the determined concentration [53]. ACI will reference ASTM C1580 for water-soluble sulfates in soils and ASTM D516 for sulfates in water.

Table 1. ACI C318-08 sulfate exposure classes

<table>
<thead>
<tr>
<th>Severity of Potential Exposure</th>
<th>Water-Soluble Sulfate (SO₄) in Soil, % mass</th>
<th>Sulfate (SO₄) in water, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>SO₄ &lt; 0.10</td>
<td>SO₄ &lt; 150</td>
</tr>
<tr>
<td>S1</td>
<td>0.10 ≤ SO₄ ≤ 0.20</td>
<td>150 ≤ SO₄ ≤ 1500 and Seawater</td>
</tr>
<tr>
<td>S2</td>
<td>0.20 ≤ SO₄ ≤ 2.00</td>
<td>1500 ≤ SO₄ ≤ 10000</td>
</tr>
<tr>
<td>S3</td>
<td>SO₄ &gt; 2.0</td>
<td>SO₄ &gt; 10000</td>
</tr>
</tbody>
</table>

Table 2. Sulfate Resistance Requirements Adapted from ACI 318-08

<table>
<thead>
<tr>
<th>Severity of Potential Exposure</th>
<th>w/cm by mass, max</th>
<th>Prescriptive Cementitious Material Requirements</th>
<th>Performance Cementitious Material Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Types of Cement</td>
<td>Maximum expansion when tested using ASTM C1012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ASTM C150 ASTM C595 ASTM C1157</td>
<td>At 6 Months At 12 Months At 18 Months</td>
</tr>
<tr>
<td>S0</td>
<td>No w/cm restriction</td>
<td>No Special Requirements</td>
<td>No Special Requirements</td>
</tr>
<tr>
<td>S1</td>
<td>0.50‡</td>
<td>Type II*† IP (MS), IS (&lt;70) (MS)</td>
<td>MS</td>
</tr>
<tr>
<td>S2</td>
<td>0.45‡</td>
<td>Type V‡ IP (HS) IS (&lt;70)(HS)</td>
<td>HS</td>
</tr>
<tr>
<td>S3</td>
<td>0.45‡</td>
<td>Type V plus pozzolan or slag</td>
<td>IP (HS) + pozzolan or slag or IS (&lt;70)(HS) + pozzolan or slag</td>
</tr>
</tbody>
</table>
2.4 Possible Test Methods to Address the Different Types of Sulfate Attack

The common element to improve resistance to any form of sulfate attack is to design the concrete to reduce the rate of sulfate ingress. While most standards limit w/c or w/cm as an indirect way of limiting the permeability of concrete to aggressive solutions, that does not mean that all types of concrete will have equal permeability at equal w/cm. Prior to the use of water-reducing admixtures and supplementary cementing materials or blended cements, this approach might have been valid, but now, a concrete can be made less permeable at a given w/cm by use of water reducing or superplasticizing admixtures which act to reduce the unit water content of the concrete, thus reducing the paste fraction and lowering porosity and permeability [54]. As well, pozzolans or slag as part of the cementitious matrix in most cases will significantly reduce permeability. Therefore, it would seem more logical to replace maximum w/cm limits with maximum limits on permeability. Many fluid or ionic transport tests are time consuming and expensive, so it would be easier to use a rapid index test that determined values that related to permeability. In the CSA A23.1 concrete standard, the ASTM C1202 rapid resistance to chloride penetration test is used for concretes exposed to aggressive chemicals using a limit of 1500 coulombs at 56 days of age for concretes that otherwise have maximum w/cm = 0.40 and 35 MPa strength. ACI is considering a similar approach [55]. Other rapid tests such as a bulk resistivity test or the NordTest NTBuild 492 rapid migration test could be equally well considered. Even though all these tests were originally designed as rapid methods to evaluate a concrete’s resistance to chloride penetration, they would apply equally well as indicators of sulfate ingress. A modification of ASTM C1202 was already suggested by Timidajski and Turc [56] for evaluation of sulfate resistance.

Once a test limit is placed on the permeability of the concrete, then a series of tests could be performed to evaluate the chemical resistance of the cementitious materials to the various types of sulfate attack are needed. It would be advantageous to use a single paste or mortar mix and cast single types of specimens that can then be placed in the required suite of environments. Specimens such as the ASTM C1012 bars, the Wittekindt [14] thin mortar bars or even the NIST mini paste prisms [10] could be used and exposed to solutions of sodium and magnesium sulfate at both 23°C and 5°C, with expansion or visual deterioration used as failure criteria. This would generally address both the ettringite and thaumasite forms of attack. As stated previously, physical sulfate attack will be minimized by limiting the w/cm or the permeability. But to prove the concept, a test program is needed where the rapid tests are evaluated against long-term performance of concretes, made with a range of w/cm, permeabilities and cementing materials, exposed to environments simulating the various forms of sulfate attack, some of which is being currently done [12].
2.5 Limitations of Test Methods

The attributes of a good test method include, (a) reliability, (b) reproducibility, (c) that it addresses a relevant performance issue (d) uses realistic boundary conditions, and (e) it is rapid and as simple as practical without overly sacrificing the other criteria.

However, it must be realized that while a test may generally address a relevant performance concern, it typically cannot mimic all relevant boundary conditions and in-situ scenarios. For example, most sulphate resistance tests only measure the resistance of a cementitious binder (typically in a mortar sample) when fully immersed in a sulphate solution (eg ASTM C1012 or the German thin mortar bar test). While these tests are relevant to the ettringite form of sulphate distress from attack on the cement aluminates, they do not relate to situations such as, (a) where the concrete is also exposed to evaporative transport (eg. physical sulphate salt crystallization pressures such as from the reversible mirabilite-thenardite transformations), or (b) where concretes are exposed to cool temperatures and carbonation favour formation of thaumasite sulphate attack on the C-S-H matrix, or (c) where different types of sulphate salts and concentration levels, than those tested, are experienced. Many of these issues are currently being addressed by members of the Nanocem consortium in Europe, after the European Cement industry could not come to agreement on a standard for sulfate resistance in 2003 [57].

However, it is doubtful that a single test could address all of these issues, and testing for all possible exposures would be both cost and time prohibitive. Thermodynamic calculations have been used to predict the phase assemblages that would occur for different starting materials placed in different solutions at different temperatures [58, 59]. This could then be used to determine appropriate test methods, or potentially in lieu of them. Development of predictive models, combined with rapid index tests and making use of relevant performance databases may provide useful solutions eventually. Predictive models will likely shape the future of standard development, when used with specific materials characterization and science-based index tests. For example, the STADIUM model [59, 60, 61] is being used to predict resistance to various forms of chloride and sulphate penetration, by modelling of the transport and interaction of multiple ionic species in solution with the solid phases. As well, a sulfate damage model has been developed by Tixier and Mobasher [62, 63]. While models maybe difficult to include directly in standards and building codes, they could be used to develop a more rationale set of requirements than simply using sulfate ion concentrations as the method of exposure classification, and for selection of appropriate materials options for use in standards.

3. SUMMARY AND CONCLUSIONS

While test methods exist that can assess resistance of cementitious materials to some of the forms of sulfate attack, these tests are generally slow and do not address the impacts of different concentrations and types of sulfate solutions. Currently, standard concrete specifications also rely on prescriptive limits on maximum w/cm (eg. ACI 318, CSA A23.1 and EN206) and in some cases minimum cement contents (EN206). Given the impacts of chemical admixtures, slag and pozzolans on resistance to ingress of sulfate solutions at a given w/cm, it might be preferable to replace current w/cm limits with a rapid index test for permeability. These limits in combination with current limitations on cement types (either prescriptive restrictions on allowable cement types or
performance-based expansion/strength tests for evaluation of cementitious combinations) will
typically provide resistance to both sulfate attack on cement aluminate phases and to physical
sulfate attack. However, they will not necessarily prevent thaumasite sulfate attack or DEF.
However, the risk of DEF can be minimized by controlling concrete curing temperatures or by use
of an alumina-bearing pozzolan or slag. In addition to limiting the permeability of concrete to
carbonation and ingress of sulfates, the resistance of cementitious materials to the thaumasite form
of sulfate attack can potentially be addressed by subjecting standard mortar bars such as ASTM
C1012 or the German thin-mortar bars to low temperature exposure. Use of slag cements also
appears to help minimize the risk of thaumasite formation. Models offer the possibility of evaluation
of a wider range of exposure conditions, and the results of models could be used to improve current
standards and building codes.

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