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Fact sheet 6
Risk of degradation from an External Sulphate Attack (ESA)

1. Introduction

This degradation risk affects concrete that is exposed to an environment rich in soluble sulphates.
There are several types of external sulphate reaction. The first kind of reaction leads to the formation of secondary expansive ettringite. The second kind of reaction, which is quite uncommon, leads to the formation of thaumasite. There can also be purely physical degradation due to salt crystallisation. Only the first reaction will be discussed in this document.

2. Consequences

This degradation can create a wide and varied range of disruptions:

- swelling.
- cracking on several scales: scaling, surface flaking, or blister (craters with localised scaling).
- in the worst case, concrete may lose cohesion.

Many of the disorders affect parts of structures that are barely or not at all accessible (foundations, pipelines, etc.), which probably leads us to underestimate their occurrence.

3. Physiochemical mechanisms

The rate at which these problems appear and grow as well as where their locations are highly variable. Such problems often remain relatively superficial (a few centimetres in depth), but they can affect a large area of the concrete protective layer covering the metallic reinforcements. Stopping reactions or even repairing the reacted material remain a challenge once degradation has started.

The mechanisms associated with ESA have not yet been established with certainty, but with our current level of understanding, we can propose the following steps for Portland cement-based concretes.

1. In the first days of the material's hydration, calcium monosulfoaluminate macro-crystals and crystallites form within the C-S-H hydrates from a combination of C_3A and the sulphates present in the binder.
2. Sulphate ions from the environments penetrate the material following two modes of transport: by diffusion when the material is saturated with water, or by advection when the material is under a hydraulic pressure gradient or during wetting/drying cycles. Surface cracking of the concrete also accelerates ion ingress.
3. These sulphate ions react with the monosulfoaluminate crystallites, which slowly transform into ettringite crystallites (calcium trisulfoaluminate). Depending on the *supersaturation* levels reached on a localised level and on confinement conditions, the formation of ettringite creates stresses that can lead to paste damage and a loss of bond between the paste and the aggregate. The calcium monosulfoaluminate macro-crystals also transform into ettringite, but it seems they do not cause such problems. Over time, some ettringite crystallites dissolve and large ettringite crystals form in the interfacial transition zone between the paste/the aggregate opened up by the previous step, increasing the disorder. At high sulphate concentrations, the formation of gypsum has also been observed.

The presence of hydraulic or pozzolan mineral additions in sufficient quantities often helps to reduce these disorders. Though the reason why is still poorly understood, calcareous fillers seem to accelerate degradation. The fineness of cement, the size of the concrete structure, and its geometry also seem to influence the rate of the swelling. Even if a material is resistant to sea water, that does not mean that it will also be resistant to sulphates.

Sea water and chlorinated de-icing salts contain soluble sulphates, but there is a competition between the fixation of sulphates and that of chlorides in the aluminate phases. The soluble sulphates can be the result of the oxidation of iron sulphides.

4. Main prediction models

There is no agreed-upon predictive model (as of 2015).

5. Influential parameters

"Material" parameters:

- Cement mineralogy: C_3A concentrations for Portland cements (*the concentration of C_4AF can also play a role*), concentration of C_3S and alkalis.

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- Type and concentration of the main hydraulic or pozzolan components in the cement or mineral additions in the concrete.
- Concrete's water/binder ratio and other factors may affect the material's final compacity (the compacity of the granular skeleton, the concrete placing, its curing, etc.)
- Size and geometry of the test samples.

For more details on the influential parameters for traditional concretes, please refer to the GRANDUBE work group's bibliographical review "Endogenic reactions" [9].

"Environment" parameters:

- The sulphate ion concentration at the concrete's surface as well as the type of associated cation (Ca^{2+}, Na^{+}, Mg^{2+}).
    - o Degradation in the presence of magnesium sulphate is generally more pronounced for Portland cement-based materials (C-S-H degrades into "M-S-H", which has no binding property).
- The rate of sulphate ion renewal at the concrete's surface.
- The frequency of wetting/drying cycles at the concrete's surface, when these cycles have a significant impact on the water saturation degree of the first few centimetres of the concrete surface.
- The temperature.

6. Testing method stages

Tests can be divided into qualitative binder assessment tests, generally carried out on mortars (test samples are 2x2x16 or smaller, thin plates, etc.), and concrete performance tests, carried out on prisms, cylinders, or cores. The smaller the sample, the faster the test.

Tests generally follow the same outline:

- moist curing of the test sample.
- immersion in a sulphate solution at 20-23°C depending on the country.

These tests are often long (several months for mortar, sometimes several years for concrete). To accelerate the degradation process, some tests include:

- cycles of drying and immersion of test samples.
- a drying phase followed by a single saturation in a vacuum using the sulphate solution at the beginning of the test.

Most tests use Na_2SO_4 solutions, with concentrations that range from 16-33 g of So_4/l. Some tests use a less concentrated solution, which makes the test longer if no other means of accelerating reactions is used. Magnesium sulphate is more aggressive. Gypsum is markedly less soluble and leads to longer test durations. The salt to be used may be chosen based on the environmental conditions planned for the material to be tested.

For some tests, the pH of the sulphate solution is regulated, which speeds up the test and makes it more representative of mediums with constant compositions. In many tests, in order to maintain the most constant sulphate levels possible throughout the test (since the material consumes sulphate), the sulphate solution is renewed regularly (often when measurements are taken). A large solution / material volume ratio is also recommended.

The measured quantities of interest are:

- the longitudinal deformation and the mass of test samples.
- but also sometimes the mass of scales produced, the density, strength, dynamic elasticity, or the flux of leached materials.

7. Standard testing methods

Today, there is a wide rage of possible tests, but very few have lead to any kind of consensus.

Tests listed in current rules for on-site use with conventional concrete:

Name	Curing	Sample	Immersion conditions	Test duration	Quantity	Comment
CSA A3004-C8 - Procedure A [1] and ASTM C1012 :2013 [3]	Under water until Rc>20MPa	Mortar strips of 2.5*2.5*28.5 cm	$[SO_4^{2-}]$ = 2.8 g/l (Na_2SO_4 solution) at 20°C	12 or 24 months	expansion	
SIA 262/1:2013 [4] appendix D	28 day under water.	28mm diameter 150m concrete core	4 cycles of 2 days of drying and 5 days in a 33 g SO_4^{2-}/l	56 days	expansion and mass	Concrete performance test

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			solution of Na_2SO_4			
NF P18-837 [5]	28 day under water.	Mortar strips of 2*2*16 cm	$[SO_4^{2-}]$ = 19.5 g/l ($MgSO_4$ solution) at 20°C	56 weeks	expansion	

Alternative testing methods:

Cur Recommendation 48 [6]	28 day under water.	Mortar strips of 2*2*16 cm	$[SO_4^{2-}]$ = 16 g/l (Na_2SO_4 solution) at 20°C	56 weeks	expansion	
Wittenkind Test [7]	demoulding at 2 days, then 14 days in limewater	Mortar strips of 1*4*16 cm	$[SO_4^{2-}]$ = 29.5 g/l (Na_2SO_4 solution) at 20°C and 5°C	>= 7 months	expansion and dynamic elasticity modulus	Control sample in limewater recommended

Other methods may be found in the state of the art section of document PD CEN/TR 15697-2008 [8].

8. Performance assessment

Some of these tests have thresholds for an "absolute" assessment. The reader is invited to consult the testing methods or the associated document booklets to find these thresholds. These thresholds are specific to each test; they can by no means be used for other tests before they are approved through adequate study.

9. References

[1] CAN/CSA-A3000-13 - Cementitious materials compendium, 2013, pp. 282.
[2] ASTM C 452/C 452M:2010. Standard Test Method for Potential Expansion of Portland-Cement Mortars Exposed to Sulfate., 2010.
[3] ASTM C 1012/C 1012M:2013. Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution., 2013.
[4] SIA 262/1:2013 Construction en béton - Spécifications complémentaires, 2013.
[5] NF P 18-837:1993. Produits spéciaux destinés aux constructions en béton hydraulique - Produits de calage et/ou scellement à base de liants hydrauliques - Essai de tenue à l'eau de mer et/ou à l'eau à haute teneur en sulfates., 1993.
[6] CUR-aanbevelingen 048:2010 Procedures, criteria en beproevingsmethoden voor de toetsing van de geschiktheid van nieuwe cementen voor toepassing in beton en voor de gelijkwaardige prestatie van beton met vulstoffen, 2010.
[7] Wittekindt, Sulphate-resistant cements and their testing, Zement Kalk Gyps, (1960) 565 - 572.
[8] PD CEN/TR 15697:2008. Ciment. Essais de performances relatifs à la résistance aux sulfates. État de l'art - Cement. Performance testing for sulfate resistance. State of the art report., 2008.
[9] GranDuBé, (2007) Grandeurs associées à la Durabilité des Bétons, sous la direction de G. Arliguie et H. Hornain, Presses de l'Ecole Nationale des Ponts et Chaussées, 2007.