DURABILITY OF FIELD CONCRETE MADE OF PORTLAND CEMENT AND SUPPLEMENTARY CEMENTITIOUS MATERIALS UNDER SEVERAL EUROPEAN EXPOSURE CONDITIONS

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Abstract
Deterioration of cementitious materials by sulfate ions is a concern for concrete in contact with ground water (and in a lesser extent sea water) in many parts of Europe, and is an important issue for underground construction identified as a major area for progress in the construction industry. Sulfate resistance relates closely to testing and standardization and therefore to prescriptive approaches. The lack of feed back on the durability of structures made of blended cements makes it difficult to fit these new concretes with existing test methods and performance criteria. This paper concerns the microstructural study of field samples and structures made of blended concretes available across Europe. This concerns several materials exposed to various climate regimes, ranging from Southern to Northern Europe (Spain, Germany, United Kingdom, Denmark and Norway). Complementary techniques such as SEM, micro-XRF, XRD and PIXE are used to evaluate the microstructural performance and stability of the phase assemblage of those blended concretes in the case of sulfate (and chloride in some instances) ingress, compare to pure Portland concrete.

1. INTRODUCTION
The understanding of degradation mechanisms is key to optimize concrete durability and reliability i.e. to improve the performance of structures. When exposed to wet sulfate-bearing environments e.g. sea water, fresh water or ground water with typical sulfate concentrations of 0.02-2.9 g.l⁻¹ (0.2-30 mmol.l⁻¹) and pH of 7-8, concrete structures generally experience three main kinds of macroscopic damages: expansion, softening and decohesion, all leading to a loss of strength. Most results dealing with sulfate resistance of cement are derived from accelerated laboratory tests on mortars bars. Data from sulfate induced damages of structures under field conditions are fewer and highly fragmented. At the moment there is no real link between data from accelerated laboratory experiments and the performance of field structures under sulfate attack, making life time predictions of concrete constructions difficult.
Prescriptive approach

The traditional approach to prevent sulfate attack from occurring aims at establishing prescriptions on cement composition. This approach was developed in the early 30’s with the limitation of alumina availability to avoid ettringite formation: together with a decrease of the water to cement ratio, the $C_3A$ content of cement was reduced and sulfate resisting Portland cements (SRPCs) were introduced on the market with high $C_4AF$ content to balance $C_3A$.

More recently, the increased use of mineral admixtures has lead to the introduction of new norms on cement composition to fulfill durability criteria: 5 types of cement were introduced, with 27 different possible compositions e.g.:

- CEM II / A&B-V&W types should concern high alumina fly ash although is it not established whether an increased $Al_2O_3$ content would stabilize monosulfate with respect to ettringite or not if sulfate is supplied [1]
- CEM III types should have a slag replacement higher than 65wt.-% to reduce sulfate attack since there are a lot of disagreements on the effects lower replacement levels and their consequences in the case of sulfate attack [2].

Nevertheless, owing to different habits and raw materials availability, most of the countries came to national prescriptions concerning the type of cement to be used and the w/c-ratio according to the type of exposure.

Furthermore, recent trends tend to integrate physical effect considerations in addition to chemical degradation and since expansion can occur even with low $C_3A$ cements [3], sulfate attack is indeed more complicated than purely related to ettringite formation. Compared to field results, such prescriptive approaches are therefore not flexible enough to allow preventing sulphate degradation.

Performance approach

Efficient resistance to sulphate attack implies the setting of fast, reproducible and reliable laboratory tests. So far, no harmonized CEN standard could be established: the draft for an EN test method failed because of a too large dispersion of results between test laboratories, mainly because of non-representative testing conditions [4]:

- too high sulfate concentrations compared to real conditions
- uncontrolled high pH, even if solution regularly changed according to ASTM C1012
- Interfacial Transition Zone (ITZ) influence not taken into account
- non-adapted and non-comparable curing conditions

Furthermore, the microstructural changes and degradation induced by field sulphate attack need to be accurately investigated for evaluation of accelerated lab-tests. This has been done in the case of pure Portland materials (ref) but the effects of supplementary cementitious materials (SCMs) are poorly documented so far. The aim of the present work is to start to fill the lack of the knowledge on this topic with generating qualitative and quantitative microstructural data of concrete from real structures and field exposures involving sulfate attack under different environmental regimes, ranging from Southern to Northern Europe (Spain, Germany, United Kingdom, Denmark, Norway). This implied the careful collection of selected specimens for which the nature of the cement used, mix design, cure and field exposure history are known.

2. FIELD SAMPLE SELECTION & RESEARCH STRATEGY
29 different samples have been chosen out, coming from 7 locations in Europe and exposed to 4 main different types of conditions: sea water (North sea and Atlantic Ocean), fresh water and ground water (Figure 1). The collected specimens include cores from real structures and field trial samples, made of different cements and SCMs and exposed for several ages ranging from 9 to 68 years (Table 1).

The principal expected inputs from these field samples is the measure of the depth of penetration of ingress species (mainly sulfates), the evaluation of the modification of their microstructure along this penetration profile during their service life and how it has (or not) resisted to sulphate ingress and deterioration. Eventually, diffusion profiles and coefficients of sulfates (and chlorides for sea side exposed samples) would be assessed although the ingress mechanism is reactive-diffusive rather than purely diffusive.

Ingress profiles of sulphate (and eventually chlorides) were measured using micro x-ray fluorescence (micro-XRF) elemental mappings (resolution 150 μm), proton-induced x-ray emission (PIXE - resolution 3mm), analytical chemistry (on ground slices of 5 mm) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) elemental mappings (resolution 1 μm). Micro-XRF, PIXE and SEM-EDS work on the same principle which is the measure of characteristic radiative de-excitation rays of elements excited by conventional X-rays, accelerated proton H⁺ and electrons respectively. Although these four techniques have variable resolution limits, this complementary approach help in assessing their reliability and accuracy. Phase composition and phase assemblages along the measured ingress profiles were investigated by mean of SEM-EDS, SEM-backscattered imaging on polished cross section and XRD.
### Table 1: Specimens characteristics

<table>
<thead>
<tr>
<th>Location</th>
<th>Specimen type</th>
<th>Exposure</th>
<th>Age (years)</th>
<th>Cement type(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goldisthal, D</td>
<td>tunnel (dry shotcrete)</td>
<td>ground water</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Trondheim, N</td>
<td>Field trial samples</td>
<td>sea water</td>
<td>20</td>
<td>CEMI + SF</td>
</tr>
<tr>
<td>Hirtshals Harbour, DK</td>
<td>Field trial samples</td>
<td>sea water</td>
<td>24</td>
<td>CEMI / CEMI-SR / CEMI + SF / CEMI-BV / CEMIIBV+SF / CEMI-SR+FA / CEMI-SR + FA</td>
</tr>
<tr>
<td>Uefingen, D</td>
<td>Lock</td>
<td>fresh water</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>Untertuerkheim, D</td>
<td>Dam</td>
<td>fresh water</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Huelva, SP</td>
<td>?</td>
<td>sea water</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Shipston on Stour, UK</td>
<td>Field trial samples</td>
<td>ground water</td>
<td>9</td>
<td>CEMI / CEMII-BV (FA) / CEMIIIB (slag) / CEMIALL</td>
</tr>
</tbody>
</table>

SF : silica fume / FA : fly ash / SR : sulfate resisting

### 3. CEMI vs. CEMI + SILICA FUME AT SEA WATER EXPOSURE

Concretes prisms were made with the same Portland cement without and with 10% silica fume at water to cement (/binder) ratios of 0.4 and 0.42 respectively. Mix designs were the same with a cement content of 300 kg.m$^{-3}$. Those field trial samples were exposed 24 years in marine environment at Hirtshals Harbour in Denmark. The samples were immersed in sea water which temperature varies between 7 and 16°C in the year and which average SO$_4^{2-}$ concentration is 2.65g.l$^{-1}$ at pH is about 8. Cores of 10cm in diameter were extracted from the exposed specimens in 2007.

The measured total porosity (mercury intrusion porosimetry (MIP)) of the cores was 8.15 and 7.09% (SF). The carbonation depths were measured to be 2 and 0.7 mm respectively. Figure 2 gives the XRF sulphur maps from which semi-quantitative analysis of the S/Ca ratios were extracted.

![Figure 2: Sulfate ingress in CEM I (left) vs. CEM I +SF (right) exposed 24 years to sea water (right)](image)
The PIXE measurements done in surrey (UK) allow rescaling the XRF profiles in S/Ca atomic ratios which can then be compared to sulfate titration by chemical analysis (Figure 3). All materials can then be compared on a comparative quantitative basis in terms of external species ingress. Based on those sulfur profiles, SEM microstructural analysis was performed to assess the phase assemblage and phases composition at some specific stages of the SO$_4^{2-}$ ingress profile. This was done through hundreds of SEM-EDS spot analysis of the cementitious matrix from which atomic ratios between selected elements allows identifying phases in equilibrium. Those results were complimented with X-ray diffraction (XRD) analysis of ground slices cut form the cores at selected depth along the sulfate profile. The combination of those approaches allows drawing qualitative phase assemblage diagrams as shown in Figure 4.

![Figure 3: Sulfate ingress profiles by XRF and PIXE (left) and chemical analysis (right) of CEM I exposed 24 years to marine environment](image)

![Figure 4: Qualitative phase assemblage vs. sulfate penetration depth (red line / a.u.) of CEM I (left) and CEM I +SF (right) exposed 24 years to marine environment](image)

The relative amounts of the main phases in equilibrium at various sulfate penetration depth are highly approximate since they were roughly appreciated based on EDS and XRD data. However, qualitatively those graphs allow assessing the effect of mineral additions on the microstructural changes induced by sulfate penetration. In the present case, the use of 10 wt% of silica fume significantly reduces sulfate ingress since ettringite (AFt) is observed up to 1.5
mm while 12 mm in the case of the pure Portland binder. Chloride ions penetrate much further in both systems which shows that either they are more mobile than sulfates or that sulfates much strongly bind to hydration products are diffuse much slower in the microstructure.

4. CEM I vs. CEM II / B-V (FLY ASH) AT GROUND WATER EXPOSURE

Concretes prisms made of 320 kg.m\(^{-3}\) of pure CEM I 42.5 blended with 30% of high siliceous fly ash (PFA) were cast at water to cement (/binder) ratios of 0.53 at the exposure site and buried immediately after demoulding in the ground were the averaged characteristic for the first 7 years were measured to be:
- sulphate concentration : 1.89 g.l\(^{-1}\)
- temperature : 10.7°C
- pH : 7.62

Those field trial samples were cast in 1998 and removed from site in 2007 i.e. exposed 9 years in the conditions mentioned above. Their measured total porosity by MIP was 8.2 and 7.7% (CEM II/B-V).

The same approach as in §.3. has been applied: sulfate penetration profiles are given in Figure 5 and phase assemblages in Figure 6. There again, the effect of SCMs (fly ash in the present case) are highlighted: although the levels of sulfate and their penetration depth are roughly similar, the presence of fly ash changes significantly the phase assemblage, especially at the surface of the samples which is composed of C-S-H and AFT in the case of the blend while thaumasite and huge amounts of gypsum are also observed in the pure Portland specimen.

![Figure 5: Sulfate ingress in CEM I vs. CEM II / B-V (FA) exposed 9 years to ground water](image)
5. CONCLUDING REMARKS

The approach conducted here shows that the combined use of several techniques allows assessing easily the microstructural modifications induced by sulfate ingress in Portland-SCMs blends. The phase assemblage diagrams derived from SEM, EDS and XRD data helps understanding in which extent SCMs can prevent or delay the ingress of sulfate (and other species e.g. chlorides). This first attempt will be refined and these graphs will help understanding the mechanisms by which external ions are stopped (physical vs chemical). They will then be compared to similar diagrams obtained through thermodynamic modelling (e.g. [5])

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REFERENCES

[2] Chladzynski S.and Moir G. Draft EN procedure adopted by Poland - private communication