

MICROSTRUCTURAL SURFACE DETERIORATION OF CONCRETE EXPOSED TO SEAWATER; RESULTS AFTER 2 YEARS EXPOSURE

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Introduction

This paper presents the microscopic, mineralogical and chemical changes occurring in the surface region of concrete exposed to seawater for a period of 2 years. The work, initiated in 2010, is part of a large long-term durability study where 18 concretes having different binder combinations were cast in the laboratory and at 45 maturity days submerged in the relatively cold seawater at Rødby Harbor in the southern part of Denmark. Microscopic analysis using optical fluorescence microscopy as well as SEM-EDX has been performed before the concrete was submersed, after 6 month and after 2 years of exposure.

The focus of the long-term durability project is to study the general evolution of the concrete microstructure and to establish the composition of the phase assemblages of the paste as a function of binder type and time, and to evaluate the influence of binder type on mainly sulfate, magnesium and chloride ingress and surface deterioration. The project is presently planned to proceed until 2018 and is carried out as a project under Nanocem and the Danish Expert Centre on Durability.

The combination of well documented concrete compositions, physical, chemical and structural characteristics, as well as known environmental condition makes this program unique in respect to studying the long-time durability concrete exposed to seawater exposed.

This paper presents result from selected concrete representing the main binder combinations studied.

Methods

The concrete mix designs used for this project cover normal slump concrete and SCC. Details regarding mix designs are presented in Table 1.

Table 1: Mix design of the cast concrete. Samples A, B, D, E, J, K, Basis, R, and R+FA have been analysed at all 3 test periods (28 days, 6 months and 2 years) and these data are presented in the paper. The rest of the samples are either only analysed after 28 days or at both 28 days and 6 months.

Sample #	Cement	Concrete type	FA%	SF%	Slag%	Air Entr.	W/C	Exposure condition	Surface scaling, 2 years
A	CEM I 42,5N	Normal				+	0.40	Splash zone	Intact
B	CEM I 42,5N	Normal	15			+	0.40	Splash zone	Intact
C	CEM I 42,5N	Normal	25			+	0.40	Splash zone	Minor
D	CEM I 42,5N	SCC	25			+	0.40	Splash zone	Scaled
E	CEM I 42,5N	Normal		4		+	0.40	Splash zone	Minor
F	CEM I 42,5N	Normal	12	4		+	0.40	Splash zone	Scaled
G	CEM I 42,5N	Normal	12	4		-	0.40	Splash zone	Minor
H	CEM I 42,5N	Normal	12	4		+	0.45	Splash zone	Minor
I	CEM I 42,5N	Normal	12	4		+	0.35	Splash zone	Scaled
J	CEM I 42,5N	SCC	12	4		+	0.40	Splash zone	Scaled
K	CEM III/B	Normal				+	0.40	Splash zone	Scaled
L	CEM III/B	Normal				-	0.40	Splash zone	Scaled
M	CEM III/B	SCC				+	0.40	Splash zone	Scaled
N	CEM I 52,5N	Normal			30	+	0.40	Splash zone	Scaled
O	CEM I 42,5N	Normal		4		SAP	0.40	Splash zone	Scaled
Basis	CEM II/A-LL 52,5	Normal				+	0.40	3m below sealevel	
Rapid	CEM I 52,5	Normal				+	0.40	3m below sealevel	
Rapid+FA	CEM I 52,5	Normal	30			+	0.40	3m below sealevel	

Abbreviations: SAP super absorbing polymers

The concrete were analysed using optical fluorescence microscopy and SEM-EDX at an age of 28 days before exposure to seawater, as well as after 6 months and 2 years of exposure. From each of the concrete one fluorescent impregnated plane section covering the outer 200mm and 2 thin- and 2 polished sections were prepared covering the outer approximately 120mm of the concrete. Preparation techniques are described in Detwiler et al. (2001), Jakobsen et al. (2000).

Plane sections were examined using a stereo microscope equipped with fluorescent light. Thin sections were analysed using an optical polarizing microscope equipped with a fluorescent facility. Polished sections were analysed in a Quanta 400 ESEM from FEI equipped with a Thermo SNN analysis unit. The analysis conditions were typically HV, 20kV and a spot size 5. The samples were carbon coated.

During SEM-EDX analysis chemical traverses from the surface to about 120mm were obtained by analysing the outer hydration product (OH) of about 40 points. The points were very close to each other (micron-steps) in the outer few mm of the concrete, whereas the distance between points were increased with depth. Based on the chemical trends obtained from these traverses different levels of interests, typical 3-5 levels were further analysed. The levels analysed were typically increased in Mg, or S or Cl. At each level about 300 analyses in OH were performed. Data from these detailed analyses are not presented here.

Results

Observation from optical microscopy

The surfaces of the concrete, except for Concrete A and B, all show signs of weak scaling (Figure 1) after 2 years of exposure to seawater. Often the paste at the surface is carbonated (Figure 2) and air voids more or less filled with calcite is observed. Based on mineralogy and morphology of phases the optical microscopy observations show very clearly that the concrete can be divided into different zones inwards from the exposed surface (Figures 2 and 3). The paste of the outermost concrete, is as mentioned, carbonated. Behind the carbonated paste a zone completely black in X-polarised light appears. This zone is apparently relatively dense (dark green in fluorescent light) and rich in short, brittle cracks having no preferred orientation (Figure 4). The zone is gradually replaced by another zone with a somewhat black, but distinct opaline paste where calcium hydroxide is present but almost invisible due to the opaline shine. The interface between the cracked zone and the opaline zone is usually marked by porous paste containing small rounded calcite rosettes, the so called popcorn carbonation. The air voids of the opaline zone occasionally contain gypsum (Figure 5) and a thaumasite-like phase (Figure 6). Ettringite is distinct in air voids especially of the opaline zone, but occurs throughout the concrete with a decreasing amount at greater depth. Behind the opaline zone the paste looks “normal” with well distributed CH and well hydrated paste.

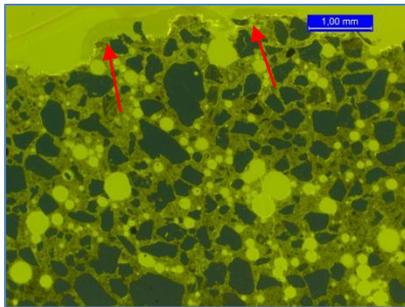


Figure 1: Example of weakly scaled surface. Fluorescent light mode.

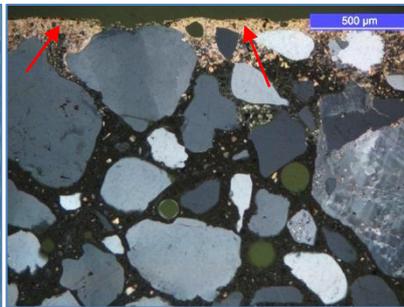


Figure 2: Carbonated paste at the surface is recognized from the brownish colour. X-polarised light-

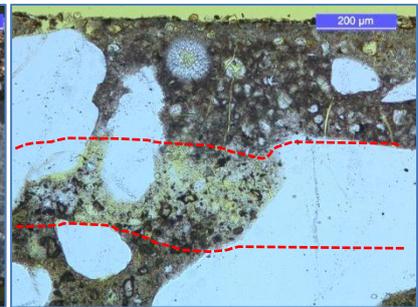


Figure 3: Distinct zoning of the surface region of the concrete. Polarised light.

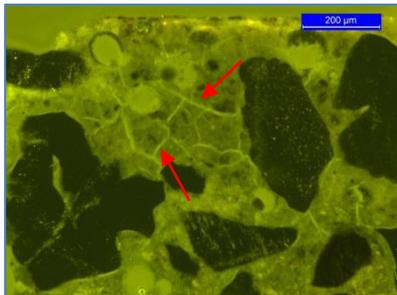


Figure 4: The outer zone of the concrete is rich in short brittle cracks. Fluorescent light mode.



Figure 5: Occasionally air voids in the surface region are filled with gypsum. X-polarised light-



Figure 6: In other occasions thaumasite-like phases are present in the air voids.

Generally the concrete contains only few cracks except for the brittle ones at the surface (Figure 4). Few fine (10-100µm wide) cracks are observed from the surface into the concrete to depths of max. 12mm; most of these appears to have formed when the concrete was relatively young.

SEM-EDX analysis

In order to add more information about the surface changes seen during optical microscopy the concrete were further analysed using SEM-EDX. This analysis shows that the surfaces of all the examined concrete distinctly can be divided into 3 chemical zones (Figure 7), three zones which coincide with the optical observations. The zones are defined based on atomic%, Mg-zone >0.5, S-zone 1.5-3.5, and Cl-zone 0.75-4 atomic%.

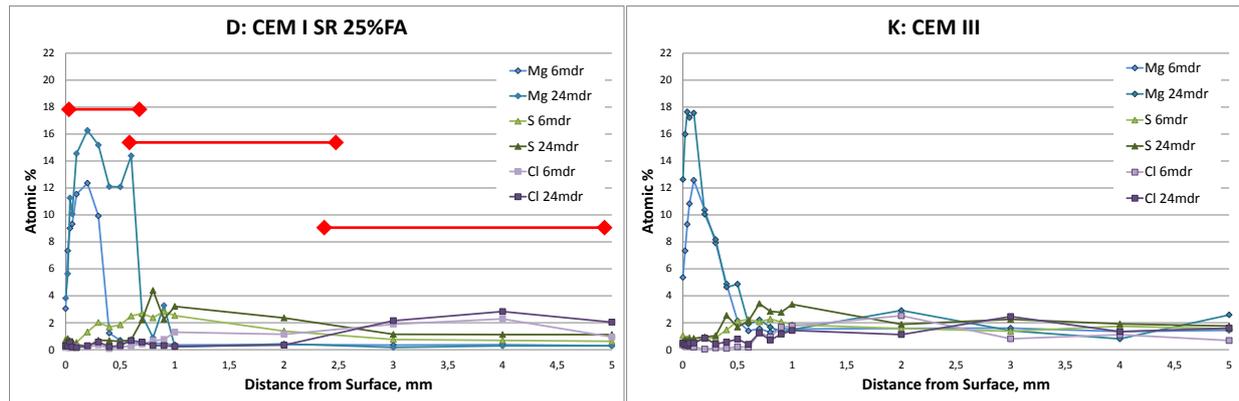


Figure 7: Examples from Concrete D and K of the variation of Mg, S and Cl with depth and exposure time. The red bars indicate the position and extend of the 3 zones (the chloride-zone is deeper than shown on the Figure, where the x-axis is cut off at 5mm).

The zoning observed (mineralogical as well as chemical) was in most of the samples already observed after 6 month of exposure; after 2 years the zoning is more distinct in some of the concrete, while in others only little progressions is observed (Table 2). The zoning can be divided into 3 main zones (Figure 7); the outermost typically less than 1mm deep is enriched in magnesium and silicon, Mg and Si. The second zone to maximum of 13mm in depth is enriched in sulphur, S. The third zone is enriched in chloride, Cl (>0.75 atomic%), and can in one concrete be traced to a depth of 70mm. The 3 zones show only a slight overlap with each other.

Table 2: Depth/thickness of distinct zones observed by SEM-EDX, depths are in mm from exposed surface. *Concrete A and B had intact surfaces after 2 years of exposure; the other concrete surfaces were slightly scaled. Maximum depths of zones are highlighted.

Concrete	Binder	Mg zone		S zone		Cl zone	
		6 months	2 years	6 months	2 years	6 months	2 years
A*	CEM I SR	0.3	0.2	0.2-2	0.3-1	0.4-20	0.3-70
B*	CEM I SR, 15%FA	0.4	0.2	0.3-1	0.02-1	0.6-15	0.02-20
D	CEM I SR, 25% FA	0.3	0.9	0.2-2	0.7-2	0.8-13	3.0-15
E	CEM I SR, 4% SF	0.2	0.7	0.2-2	0.5-5	0.4-13	4.0-20
J	CEM I SR, 12%FA, 4%SF	0.7	1.0	0.7-3	0.8-3	2.0-13	3.0-13
K	CEM III/B	0.4	0.5	0.4-1	0.3-13	0.7-5	0.7-6
Basis	CEM II/A-LL	0.3	0.2	0.1-1	0.2-1	0.5-15	0.9-20
Rapid	CEM I, 52.5		0.4		0.4-4		0.6-33
R+FA	CEM I, 52.5, 30% FA		0.3		0.3-1		2.0-13

Typically none of the concretes show sign of brucite, MgOH₂, precipitation at the surface, except for concrete B containing 15% FA which after 2 years of exposure was partly covered by brucite. All the other concrete shows after 2 years a max. 1mm cracked zone in the surface (Figure 8) where the paste is more or less decalcified. This zone appears to be equal to the observed black zone observed in X-polarized light. The zone consists almost exclusively of Mg and Si. Plotting the atomic ratios of Al/Ca versus the Mg/Ca show that the paste of this zone consist of a magnesium silicate hydrate, except for in concrete K (CEM III/B) and in concrete Basis (CEM II/A-LL) where the main phase is hydrotalcite. The calcite popcorns at the interface to the S-zone corresponding to the opaline zone in X-polarised light are also observed in backscatter mode (Figure 9). The S-zone varies slightly

in thickness, the thinnest zones are found in concrete A, B, Basis and Rapid+FA; the thickest zone of 13mm in concrete K containing pure CEM III/B. The S-zone contains a relative high amount of ettringite in the paste (in relicts after hydrated cement grains), in air voids and in few small cracks (Figure 10). The infilling of the relicts after hydrated cement grains causes the opaline shine of the paste observed in X-polarised light as the light coming through the specimen is spread due to the presence of the minute small S-phases all over the paste. When the concentration of S decreases and ettringite becomes more difficult to observe within the paste, EDX analysis shows an increase of the chloride content (> 0.75 atomic%). The thickness of the Cl-zone varies from concrete to concrete being thinnest in the CEM III/B concrete and thickest in the concrete containing only CEM I (Table 2). Both optical microscopy and SEM-EDX analysis shows a distinct presence of Friedel's salt in relicts after cement grains in the Cl-zone, especially at larger depths.

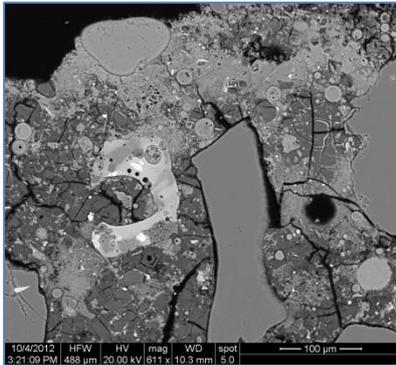


Figure 8: Example of deteriorated surface. The paste consists of mainly Mg-Si (dark grey) and areas of calcite. The zone is distinctly cracked and the surface is scaled. CEM I SR concrete with FA and SF. Backscatter image.

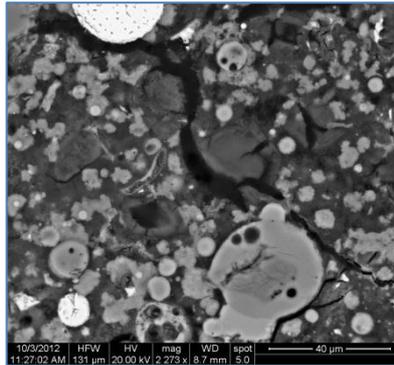


Figure 9: Typical appearance of the popcorn carbonated zone between Mg- and S-zones. "Popcorn" appears as small light grey irregular spots (not to be confused with the spherical fly ash particles). CEM I SR concrete with FA. Backscatter image.

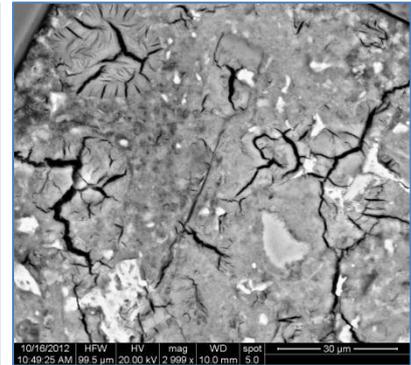


Figure 10: The S-zone behind the Mg-zone is highly enriched in ettringite in e.g. air voids and relicts after cement grains. This zone occasionally contains thaumasite and gypsum in air voids. Note the cracking of ettringite is an artefact which forms in the SEM due to dehydration/shrinkage of the H₂O-rich phase. Concrete with pure CEM I 52.5. Backscatter image.

Discussion and Conclusion

The study concerning the influence of seawater on various concrete types shows that the concrete surfaces changes in a morphological, mineralogical, and chemical way. After 2 years of exposure distinct zones (though they are on a microscopic scale) are observed within the surface region. The depth of the zones seems to depend on binder type and to a certain extent on time. The two outermost zones are both visible in the optical microscope as well as in the scanning electron microscope, where they from the surface represent a decalcified Mg-Si zone followed by a S-zone rich in various sulphate phases appearing in the microstructure. One more zone is recognised but only by use of the SEM-EDX analysis. In this Cl-zone located behind the S-zone, Friedel's salt is occasionally observed in relict after hydrated cement grains and where Cl is bound in CSH.

The broadest Mg-zone of about 1mm are found in concrete D, E and J (Table 2), which is concrete based on CEM I SR cement, FA or SF or a combination of the two pozzolans. There is a clear broadening of the zone from 6 months exposure to 24 months. The zone is also observed in the other concretes but is much thinner and it seems like the zone has not broadened from 6-24 months of exposure.

The broadest S-zone is observed in concrete K containing CEM III/B (slag), where the S-zone reaches a depth of 13mm. In concrete E containing CEM I SR cement and SF it reaches 5mm and in concrete Rapid containing CEM I, 52.5 it reaches 4mm.

The Cl-zone can be traced to the deepest level in concrete A with pure CEM I SR cement (70mm) and in concrete Rapid with pure CEM I 52,5 cement (33mm) (Figure 8). Only in concrete A an increase of the depth of the zone is seen from 6 to 24 months, it increases from 20 to 70mm. In the rest of the concretes the Cl-enrichment are observed to depth of max. 20mm and almost no changes are observed from 6-24 months.

The ingress of seawater seems to influence the surface durability by especially the creation of a magnesium silicate hydrate (M-S-H) zone. The concrete becomes decalcified and cracked, resulting in scaling of the surface. The observation of this zone is not unusual and it is also observed in a recent study on up to 35 years old Danish bridges (data not published yet but uploaded here <http://www.concreteexpertcentre.dk/32859>), but it

is surprisingly in contrast to the observations obtained by Chabrelie et al., (2008) on concrete from an exposure site in Northern Denmark.

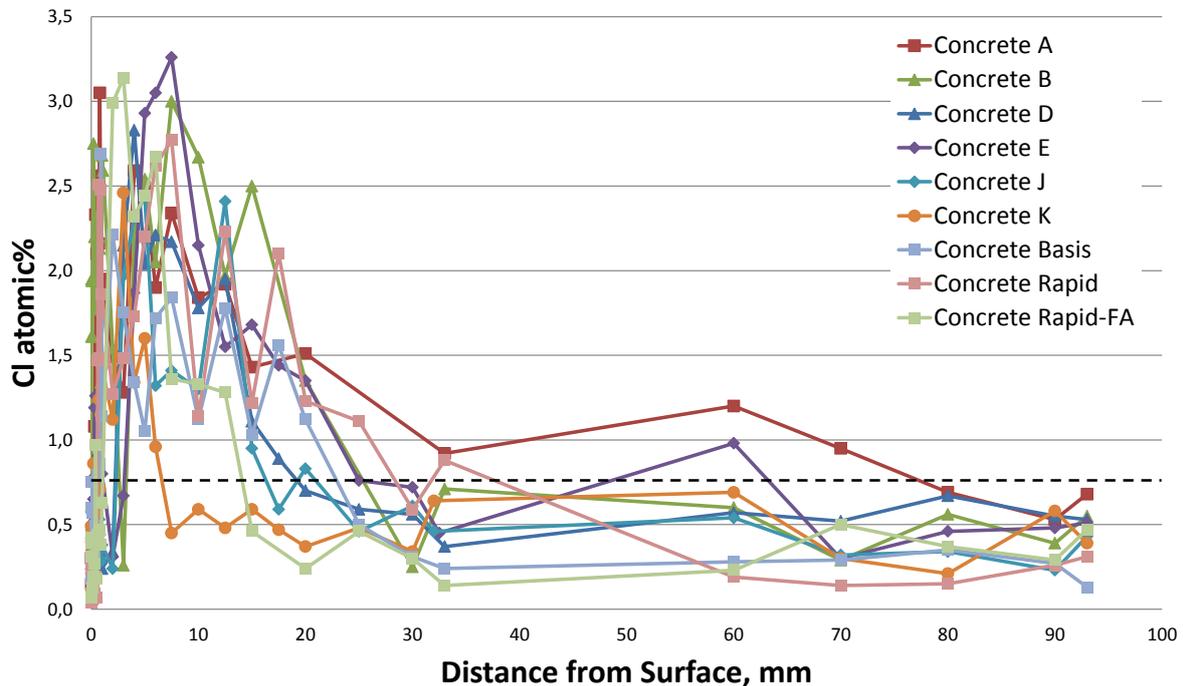


Figure 8: Cl-profiles after 24 months of exposure for the 9 examined concretes. The Cl-background values of non-exposed concrete are indicated with a stippled line. The Cl-content of concrete A does not drop under the background level before a depth of >70mm.

Here they did not find this zone instead they found a dense brucite layer on the surface which they suggest have protected the concrete from magnesium penetration into the concrete. The concrete examined in that study contained similar cement as used in the concrete of the Old Danish bridges and in the Femern trial concrete.

As expected S is contrary to Mg transported to deeper levels of the concrete but except for a slight decalcification of this zone no sign of damage is presently related to the S-build up. Formation of gypsum and thaumasite is however observed, but at this stage it is only filling air voids. Gypsum and thaumasite is also observed in the study of the Old Danish bridges but strangely not observed in the concrete examined by Chabrelie et al. It is at the moment not clear why these differences occur.

Acknowledgement

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