

Marie Helene Bjørndal

Impact of leaching on chloride ingress profiles in concrete

Master's thesis in Civil and Environmental Engineering
Supervisor: Klaartje De Weerd, Alisa Machner
December 2019

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Norwegian University of Science and Technology
Faculty of Engineering
Department of Structural Engineering

Preface

This paper is written as the final submission in the five-year master's study in Civil and Environmental engineering with specialization in concrete technology at NTNU. During the final year of the study program one has to write a specialization project, take the subject TKT4235 Concrete technology advanced course, as well as write the master's thesis.

During the year of 2019 I have had the pleasure of being included in the concrete group at NTNU, working on the EnDurCrete project (www.endurcrete.eu). EnDurCrete is an EU Horizon 2020 project, where the main goal is to develop a new cost-effective and sustainable concrete, based on low clinker cement containing high value industrial by-products. The project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 760639 "EnDurCrete".

My participation in the EnDurCrete project has included laboratory work and treatment of data from laboratory tests, as well as attending Skype meetings with project partners CEA (France) and ZAG (Slovenia). The agenda for the skype meetings has been coordinating laboratory work between NTNU and ZAG, and making sure that the results from the laboratory tests will provide the necessary and useful input for the modelling performed by CEA.

For my project work I participated in laboratory work, such as relative humidity measurements and preparation of samples for exposure in carbonation chamber during late spring 2019. For the relative humidity (RH) measurements, I contributed to creating a procedure for the experiment, calibrating the humidity sensors before and after the measurements, preparing samples and executing the measurements. After returning to NTNU at the beginning of August treatment of data from the different experiments started. I treated data from carbonation depth measurements with thymolphthalein, results from TGA, and the RH-measurements. Parallel to this, I was writing a report describing the carbonation experiments performed at NTNU in the EnDurCrete project, and determination of the carbonation resistance of the new binders introduced in the project. The report was submitted for grading 27th of September (end of week 39).

For the master thesis it was decided to present the results in the form of a scientific journal paper, which is aimed to be submitted to Materials and Structures. The work started in September 2019 and was finalized in December 2019. Besides learning how to write a paper, I have also participated in the laboratory work. I took part in potentiometric titration of profile ground concrete and mortar samples that were exposed to chloride containing solutions, where we also prepared samples for ICP-MS. I also received training in how to operate the μ XRF in the laboratory, started scans, retrieved and treated the data from the scans. In order to determine the degree of leaching in the samples, TGA was performed on all profile ground mortar samples. This took several weeks, where I had the responsibility for running the TGA some of the days. I helped prepare exposure solutions and exposed the crushed paste samples for chloride binding isotherms (not included in the paper). An overview of the work related to the master thesis is presented in a Gantt diagram on the following page.

Trondheim, December 2019.
Marie H. Bjørndal

	Week															
Task	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51
Meetings with project partners																
Laboratory work																
<i>μXRF</i>																
<i>Potentiometric titration</i>																
<i>Chloride binding isotherms</i>																
<i>TGA</i>																
Master thesis																
<i>Start working with paper</i>																
<i>Methods and materials</i>																
<i>Results</i>																
<i>Literature study</i>																
<i>Introduction</i>																
<i>Discussion/conclusion</i>																
<i>Hand-in</i>																

Acknowledgements

During the last year I have been included in discussions regarding topics of my specialization project and master's thesis, as well as topics beyond this. I would like to thank my supervisors, professor Klaartje De Weerd and postdoc Alisa Machner, for including me this way and providing me with helpful guidance and support whenever I have needed it. I have truly learnt a lot about research and gotten a taste of how it is to be a scientist at NTNU, and I am very grateful for this experience.

Abstract

Chloride induced reinforcement corrosion is one of the main deterioration mechanisms for reinforced concrete structures. Chlorides penetrate the concrete cover with time, and initiate corrosion as they reach a critical chloride content at the reinforcement surface. In this study we want to investigate the effect of leaching on chloride ingress profiles in concrete. Concrete and mortar samples were exposed for 90 days to two different exposure solutions: 3% NaCl, and 3% NaCl with additional KOH to limit leaching. The solutions were exchanged weekly. After exposure, total chloride profiles were determined to investigate the chloride ingress, as well as portlandite and potassium profiles to investigate the extent of leaching. We observed that leaching leads to considerably higher maximum total chloride contents, compared to the samples where leaching was limited (150% increase). The chloride ingress depth, however, was not greatly affected by leaching, meaning that the service life is not necessarily reduced due to leaching. Thus, total chloride profiles are mainly governed by the interaction between the solids and the chlorides. This can lead to erroneous service life prediction when using empirical models, hence mechanistic service life models should be used.

Sammendrag

Kloridinitiert armeringskorrosjon er en av hovednedbrytningsmekanismene for armerte betongkonstruksjoner. Klorider trenger igjennom betongoverdekningen over tid og forårsaker korrosjon når de når et kritisk kloridinnhold ved armerings overflaten. Betongens motstand mot kloridinntrenging er derfor avgjørende for levetiden. I denne studien ønsket vi å undersøke effekten utlekking har på kloridinntrengingsprofiler i betong. Betong- og mørtelprøver ble eksponert for to ulike eksponeringsløsninger i 90 dager: 3 % NaCl, og 3 % NaCl tilsatt KOH for å begrense utlekking. Løsningene ble byttet ut ukentlig. Etter eksponering ble kloridprofiler i prøvene bestemt, i tillegg til portlanditt- og kaliumprofiler for å bestemme graden av utlekking. Vi observerte at utlekking fører til betydelig høyere maksimalt kloridinnhold, sammenliknet med prøvene med begrenset utlekking (150 % økning). Kloridinntrengingsdybden var derimot mindre påvirket av utlekking, noe som betyr at levetiden ikke nødvendigvis blir redusert på grunn av utlekking. De totale kloridprofilene er i hovedsak styrt av kloridbinding i prøvene. Det ble demonstrert at dette kan føre til feilaktig estimering av levetid ved bruk av empiriske modeller, derfor burde mer mekanistiske levetidsmodeller tas i bruk.

List of appended papers

1. Marie Bjørndal, Alisa Machner, Klaartje De Weerdts "The impact of leaching on chloride ingress profiles" Materials and Structures 2019 (to be submitted)
2. Marie Helene Bjørndal, Alisa Machner, Klaartje De Weerdts "Ny sement for bedre miljø", Byggeindustrien, 2019, (Nr. 16), p. 66.

List of abbreviations

Abbreviations used:

C-S-H	Amorphous calcium silicate hydrate. The main hydration product of the silicate clinker phases (C_3S and C_2S). It has a variable composition and is therefore abbreviated and not given in a stoichiometric formula.
Afm	Alumina ferric monophase, derived from the monosulphate structure by the replacement of SO_4^{2-} with other anions. Replacement of aluminum with iron is possible.
CEM II	Main type of cement in EN 197-1.
CEM VI	Main type of cement not yet included in EN 197-1, to be included in new cement standard (planned to be released in 2020).
C-M	Portland composite cement of main type CEM II to be included in new cement standard (planned to be released in 2020). Describes clinker content, and combination of other main constituents.
S	Ground granulated blast-furnace slag as constituent in binder, in accordance with EN 197-1.
LL	Limestone as constituent in binder, in accordance with EN 197-1.
V	Siliceous fly ash as constituent in binder, in accordance with EN 197-1.
w/b ratio	Water-to-binder ratio (weight).
TGA	Thermogravimetric analysis.
DTG	Differential thermogravimetry.
ICP-MS	Inductively coupled plasma mass spectrometry.
XRF	X-ray fluorescence.
μ XRF	Micro X-ray fluorescence spectrometry.
SD detector	Silicon drift detector.
wt%	Weight percentage.

1. Impact of leaching on chloride ingress profiles in concrete

Marie Bjørndal, Alisa Machner, Klaartje De Weerd
To be submitted to Materials and Structures

Impact of leaching on chloride ingress profiles in concrete

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Abstract

In this study we want to investigate the effect of leaching on chloride ingress profiles in concrete. Concrete and mortar samples were exposed for 90 days to two different exposure solutions: 3% NaCl, and 3% NaCl with additional KOH to limit leaching. The solutions were exchanged weekly. After exposure, total chloride profiles were determined to investigate the chloride ingress, as well as portlandite and potassium profiles to investigate the extent of leaching. We observed that leaching leads to considerably higher maximum total chloride contents, compared to the samples where leaching was limited (150% increase). The chloride ingress depth, however, was not greatly affected by leaching, meaning that the service life is not necessarily reduced due to leaching. Thus, total chloride profiles are mainly governed by the interaction between the solids and the chlorides. This can lead to erroneous service life prediction when using empirical models, hence mechanistic service life models should be used.

Key words: chloride, service life, leaching, concrete, portlandite.

1. Introduction

The most common deterioration mechanism for reinforced concrete structures is corrosion of the reinforcement steel. For concrete structures exposed to a marine environment or deicing salts, reinforcement corrosion is generally induced by chlorides penetrating the concrete cover and enabling pitting corrosion as they reach a critical content at the steel surface. Today's society calls for sustainable structures with low carbon footprints and limited use of natural resources, that also withstands mechanical, chemical and environmental actions. Hence, the resistance of the concrete cover to chloride penetration, as well as understanding the mechanisms behind it, is crucial in order to confidently predict the service life of a reinforced concrete structure.

To assess how far chlorides have penetrated the concrete cover, chloride profiles are determined by giving the total chloride content in the concrete (e.g. in g Cl/ g concrete powder) as a function of the depth from the exposed surface. The total chloride content contains chlorides present in the pore solution, commonly referred to as free chlorides, and chlorides that interact with the cement hydrates, referred to as bound chlorides [1-9]. The bound chlorides can either be chemically bound in chloride-containing Afm phases, such as Friedel's salt or Kuzel's salt, or physically bound by accumulating the in diffusive layer of the C-S-H phase.

To assess how long it will take for the chlorides to reach a critical content at the reinforcement, service life prediction models are used. The most commonly used models for chloride ingress prediction are based on Fick's 2nd law of diffusion, e.g. Fib

bulletin 34 [10]. In these models, the error function solution of Fick's 2nd law is fitted to a measured chloride profile. The apparent diffusion coefficient and surface concentration are obtained as fitting parameters. This approach solely considers the ingress of chloride. The potential influence of the other ions present in the sea water, such as sodium, sulphate and magnesium, is omitted and leaching of ions from the pore solution, such as potassium or calcium, is not considered.

In previous studies on chloride ingress of field exposed concrete submerged in sea water, a bell-like shape in the chloride profiles was observed [11,12]. This entails that the chloride content at the surface is lower than the chloride content slightly deeper into the concrete. Such a bell-shape or "peaking-behavior" in chloride profiles has commonly been attributed to wetting and drying of the concrete, where the capillary suction of chloride containing exposure solutions leads to an accumulation of chlorides near the surface, whereas exposure to wind and precipitation may wash out chlorides at the surface [13]. This is not a valid explanation for the peaking-behavior in submerged concrete, as no wetting and drying is taking place. Others have attributed this peaking-behavior in concrete submerged to sea water to the presence of sulphate ions which compete with chloride ions for binding to the solids [14,3,15]. However, in a recent study, similar peaking behavior was observed for mortars submerged in NaCl solution as for mortars submerged in sea water [11]. So, the additional ions in the sea water do not explain the peaking behavior in submerged concrete. This led to the hypothesis that leaching is provoking this peaking-behavior, by affecting the chloride binding capacity in the concrete near the exposed surface. Leaching could thereby be the main explanation for what in engineering practice has been referred to as an age-dependent chloride surface content. This age-dependent chloride surface content is not understood and is, if considered at all, fitted with empirically determined coefficients [16], causing large deviations in the predicted service life of reinforced concrete structures.

In order to investigate the impact of leaching on chloride binding, we designed a set of experiments in which cement paste was artificially leached using HCl solution and the subsequent changes in the chloride binding capacity were investigated. [17,18]. We observed that a slight reduction in the pH (down to 12) lead to an increase in the chloride binding capacity whereas a severe decrease in the pH (down to 9) lead to a drastic reduction in the chloride binding capacity of the paste. Our hypothesis is that advanced leaching at the surface leads to dissolution of hydration phases accompanied by a drastic reduction in binding and thereby a reduced surface chloride content, whereas moderate leaching slightly deeper into the concrete leads to enhanced chloride binding and consequently increased chloride content in the concrete, thereby explaining the peaking behavior in the chloride profiles in submerged concrete.

In order to put our hypothesis to the test, we designed the experimental set-up presented in the current study. The set-up bares similarity to commonly used laboratory tests for chloride ingress in concrete [19-23]. Two parallel sets of mortar and concrete cylinders were submerged in two different exposure solutions, which were exchanged weekly over a period of 90 days. The twist in the set-up lies in the variation of the exposure solutions. The first exposure solution is a 3% NaCl solution, which has a similar chloride concentration as sea water and is commonly applied in

conventional laboratory tests [20,21,23]. The second exposure solution also contains 3% NaCl, but in addition contains KOH. The KOH concentration was aimed to mimic the KOH concentration in the pore solution of the mortar, which we predicted using thermodynamic modelling (150 mMol/L). The reason for choosing a KOH concentration similar to the concentration in the pore solution is to prevent leaching from the samples. The high potassium concentration in the exposure solution prevents potassium from leaching from the pore solution. More importantly, the high potassium concentration in the exposure solution results in a high pH, that keeps the solubility of calcium low. This reduces leaching of calcium from the samples during exposure and enables us to investigate the impact of leaching on the chloride profiles in the exposed samples.

Another alternative to limit leaching during the exposure would have been to use a portlandite ($\text{Ca}(\text{OH})_2$) saturated solution, as calcium is one of the elements that leach out of the sample into the exposure solution. However, portlandite saturated solutions have been observed to form a glazing on the surface of submerged concrete or mortar samples due to precipitation of portlandite or calcite caused by its limited solubility at high pH. This glazing can physically limit chloride ingress [24]. We therefore preferred to use KOH, which has a high solubility also at high pH, and would thereby influence the leaching only in a chemical way, not by physically clogging pores or sealing the exposed surface.

After exposure, the mortar and concrete cylinders are profile ground and total chloride profiles are determined. To assess the extent of leaching we focused on calcium, specifically portlandite ($\text{Ca}(\text{OH})_2$), as this is one of the first hydration phases to decompose upon leaching [25]. Other hydration phases will start to decompose when most of the portlandite has been dissolved [26,27]. Portlandite profiles were determined on the profile ground mortar using thermogravimetric analysis (TGA). In addition, potassium profiles were determined using inductively coupled plasma mass spectrometry (ICP-MS) as a second indication of leaching for both mortar and concrete [28,12].

2. Experimental

2.1 Materials

Mortar and concrete samples with two different binder compositions, CEM II/C-M(S-LL) and CEM VI(S-V), were investigated. The CEM II/C-M(S-LL) contains 50 wt% CEM I 52.5 R as described by EN 197-1 [29], 40 wt% ground granulated blast-furnace slag (GGBFS) and 10 wt% limestone filler. The CEM VI(S-V) contains 47 wt% CEM I 42.5 R as described by EN 197-1 [29], 43 wt% coarse GGBFS and 10 wt% fly ash. The components of the binders were separately ground. The chemical composition determined by XRF is given in Table 1. The mix design for the concrete and mortar samples is given in Table 2. The mix design is based on a C35/45 concrete with w/b ratio 0.45 for marine conditions. Concrete equivalent mortar was prepared by using the concrete mix design, excluding the gravel fractions. The amount of added water was reduced by the amount of water absorbed by the larger aggregates in concrete, hence the slightly lower effective w/b ratio of 0.43 was used for mortar as shown in Table 2. The admixtures in the mix design were used to ensure satisfactory workability for the concrete and mortars.

Table 1 Chemical composition (wt%) of CEM II/C-M(S-LL) and CEM VI (S-V) as determined by XRF, as well as the Blaine specific surface area (cm²/g).

Oxide [%]	CEM II/C-M (S-LL)	CEM VI (S-V)
LOI*	4.36	0.79
SiO ₂	24.18	31.79
Al ₂ O ₃	7.16	8.36
TiO ₂	0.56	0.37
MnO	0.10	0.09
Fe ₂ O ₃	1.39	2.05
CaO	53.67	48.72
MgO	3.23	3.56
K ₂ O	0.71	0.90
Na ₂ O	0.18	0.29
SO ₃	4.08	2.43
P ₂ O ₅	0.07	0.09
Sum	99.69	99.44
Blaine [cm ² /g]	5210	3870

*loss on ignition

Table 2 Mix compositions for mortar and concrete that were tested, including the water-to-binder ratio (w/b).

	CEM II concrete [kg/m ³]	CEM VI concrete [kg/m ³]	CEM II mortar [kg/m ³]	CEM VI mortar [kg/m ³]
CEM II / C-M (S-LL)	360	-	561.6	-
CEM VI / S-V	-	360	-	561.6
Washed sand 0/4	968	953	1510	1510
Gravel 5/10	390	384	-	-
Gravel 10/15	575	575	-	-
Superplasticizer	1.91	1.15	1.89	1.56
Sika Viscoflow	2.87	1.73	2.83	2.34
Water (added)	162	162	240.7	240.7
w/b ratio (effective)	0.45	0.45	0.43	0.43

Analytical grade NaCl and KOH (supplied by Merck) were used for the exposure solutions, as well as demineralized water (max. 0.5 mSm⁻¹ conductivity).

2.2 Sample preparation and exposure

The mortars and concretes were mixed using a planetary concrete mixer (Galleti P50) with 50 L capacity, in a laboratory at 23 °C ± 2 °C. Batches of 40 L were mixed according to the following procedure: Solid components were mixed for 20 seconds with 30 rpm before the mixer was stopped. ³/₄ of the water was added and mixed for 60 seconds at 59 rpm. The mixer was stopped to add the remaining ¹/₄ of the water, in addition to admixtures. The mix was mixed for 10 minutes at 59 rpm.

The requirement for slump ≥ 24 cm was checked, and if the requirement was fulfilled and no segregation or bleeding was observed the mixture was cast. If segregation or bleeding was observed the material was discarded. If the slump requirement was not fulfilled, water reducers were added, and the batch was mixed for additional 3 minutes. These steps were repeated until the slump was ≥ 24 cm.

The mortar and concrete samples were cast in cylindrical molds (height: 200 mm, diameter: 100 mm). The molds were filled and slightly stroked to make sure that the mold was filled properly. The cylinders were stored covered with a plastic plate in the laboratory and demolded after 1 day. After demolding, the samples were stored in a humidity chamber (95% RH, 20°C) for 21 days. Then the samples were sealed in plastic foil and cured further at 20 °C until they reached an age of 56 days.

The cylinders were sawn in two pieces, a test specimen and a sub-specimen according to EN 12390-11[23] (Figure 1). The test specimen was then pressure saturated with deionized water. Maximum 24 hours after pressure saturation, all surfaces of the test specimen, except for the sawn surface, were sealed with epoxy. After sealing, the samples were immersed in deionized water in order to completely re-saturate them before exposure.

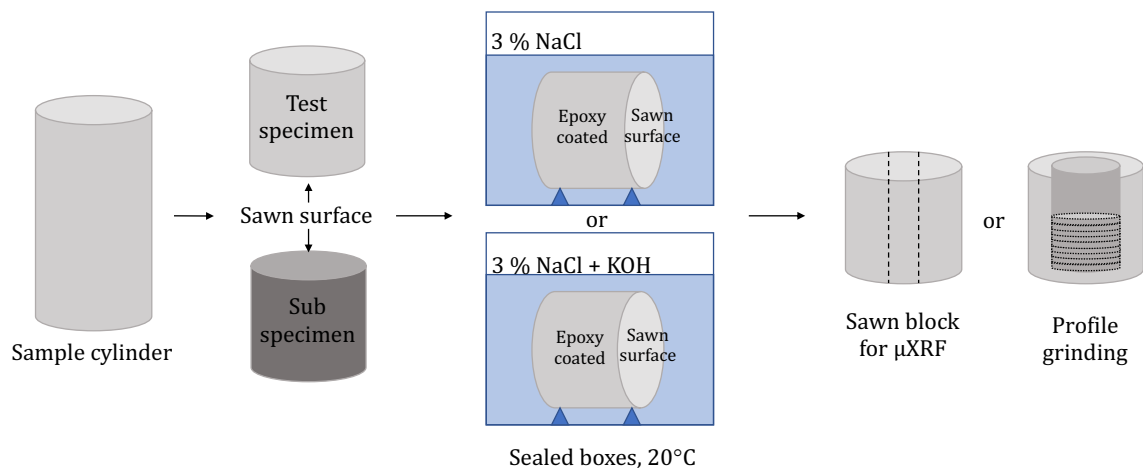


Figure 1 Sample exposure and preparation for analysis.

2.3 Exposure

The concrete and mortar test specimens were immersed in a 3 % NaCl or a 3 % NaCl+KOH solution in a sealed box at 20 °C, for 90 days. The exposure solutions were changed weekly. The 3 % NaCl solution was prepared by dissolving 30 g of NaCl in 970 g demineralized water at 20 °C. The 3 % NaCl+KOH solution was prepared by making the KOH solution before adding NaCl. The potassium content in the pore solution was modelled for the CEM II/C-M(S-LL) using the Gibbs free energy minimization software GEMS [30,31], giving a concentration of 150 mMol/L after 150 days of hydration. To reach this KOH concentration, 8.416 g KOH was dissolved in 1000 g deionized water. After preparing the KOH solution, 30 g NaCl was dissolved in 970 g of the KOH solution.

Twin samples were prepared for all samples. After 90 days of exposure, one of the twin samples was sawn into a block for scanning with μ XRF, while the other twin sample was profile ground in alignment with EN 12390-11[23](Figure 1). All samples for profile grinding were ground in 8 steps up to about 20 mm, except for CEM II mortar and concrete samples exposed to NaCl+KOH solution that were ground in 5 steps up to about 10 mm. The length of each step was measured with an accuracy of 0.1 mm.

2.4 Scanning with μ XRF on sawn samples

μ XRF scanning of mortar and concrete samples was performed to visually determine the chloride ingress depth. The scans were performed with a M4 Tornado μ XRF from Bruker, with an Ag X-ray tube with spot size 20 μ m and SD detector.

Detailed scans were performed from the exposed surface up to approximately 15 mm inwards on each sample. The distance between the measurements was set to 25 μ m, with a measuring time of 3 ms/pixel. The X-ray tube was operated at 50kV/600 μ A, with vacuum at 20 mbar and the SD detector switched on. The scans provided a qualitative description of the space-resolved presence of different elements from the exposed surface inwards, presented as elemental maps. Chloride maps were obtained for all samples.

2.5 Analysis of profile ground mortar and concrete samples

From each profile ground section approx. 5 g of powder was weighed in glass beakers, dried overnight at 105 °C and weighed again after drying in order to determine the moisture content in each section. The dried powder was dissolved in 50 ml of HNO₃ (65% diluted 1:10) heated to 80 °C and filtrated after 1 hour. The chloride content in the resulting filtrate was determined by potentiometric titration against a 0.01 mol/L AgNO₃ solution using a Metrohm Titrando 905 titrator. The chloride content for each sample as wt% of concrete or mortar dried at 105 °C is calculated by using Equation 1.

$$Cl\% = \frac{V_{AgNO_3} \cdot c_{AgNO_3} \cdot M(Cl) \cdot V_{HNO_3} \cdot 0.001}{V_{sample} \cdot m_{concrete/mortar} \cdot \left(1 - \frac{moist\ cont}{100}\right)} \cdot 100 \quad (1)$$

V_{AgNO_3} and c_{AgNO_3} represent the volume (mL) and concentration of the AgNO₃ solution (0.01 mol/L). $M(Cl)$ is the molar mass of chlorine (35.45 g/mol). V_{HNO_3} is the volume of diluted HNO₃ used to dissolve the profile ground and dried samples (50 mL). V_{sample} is the volume of dissolved and filtered sample used for the titration (1-10 mL), $m_{concrete/mortar}$ is the mass of profile ground sample weighed in (5 g), and $moist\ cont$ is the moisture content determined for each sample (about 3 wt% for concrete and 6 wt% for mortar).

The filtrate from the acid digested profile ground powder produced for the chloride

analysis was also used for inductively coupled plasma mass spectrometry (ICP-MS) analysis. The total content of potassium (K) was determined using an ICP-MS Element 2 from Thermo Scientific. The concentrations of the elements measured were recalculated relative to the dry sample mass (sample weight after drying at 105 °C).

In order to describe the degree of leaching in the samples, portlandite (Ca(OH)_2) profiles were obtained using thermogravimetric analysis (TGA). Portlandite profiles were only determined for the mortar samples, it was not done on the concrete samples. The TGA was performed using a Mettler Toledo TGA/DSC 3+, on homogenized profile ground sections from each mortar sample. Approximately 300 mg of each sample were poured into corundum crucibles. The samples were heated from 40°C to 900°C at a rate of 10°C/min, while the oven was purged with 50 ml/min N_2 . The sample weight was monitored as a function of the temperature (TG-curves). The different phases were detected by dividing the first derivative of the TG-curves (DTG-curves) into several temperature intervals as suggested by Lothenbach et al. [32]. The first peak appears at about 100 °C, as ettringite decomposes and dehydroxylation of C-S-H starts. C-S-H gradually decomposes as the temperature increases from 50 °C to 600 °C. The decomposition of portlandite takes place between approximately 400 °C and 500 °C. Carbonate decomposes at temperatures higher than 600 °C. The portlandite content was calculated by Equation 2, where w_{400} , w_{500} and w_{900} represent the sample weight at 400 °C, 500 °C and 900 °C respectively and $M(\text{Ca(OH)}_2)$ and $M(\text{H}_2\text{O})$ the molar masses of portlandite (74 g/mol) and water (18 g/mol).

$$\text{Ca(OH)}_2\text{wt}\% = \frac{w_{400} - w_{500}}{w_{900}} \cdot \frac{M(\text{Ca(OH)}_2)}{M(\text{H}_2\text{O})} \quad (2)$$

3. Results

3.1 Portlandite profiles from TGA

Figure 2 shows the portlandite (Ca(OH)_2) content in the different profile ground sections of the mortar samples prepared with the CEM II and the CEM VI as a function of the depth from the exposed surface. The samples show a similar portlandite content at higher depths (7 mm or 10 mm depending on the binder) independently of the exposure solution. Towards the exposed surface, the samples exposed to a 3 % NaCl solution show a clear decrease in the portlandite content, showing that no portlandite is present in the outermost section. The portlandite content in the samples exposed to 3 % NaCl+KOH solution also decreases towards the exposed surface, however, to a considerably smaller degree compared to the samples exposed to a 3 % NaCl solution. This indicates that the samples exposed to NaCl are leached to a greater extent than the samples exposed to NaCl+KOH.

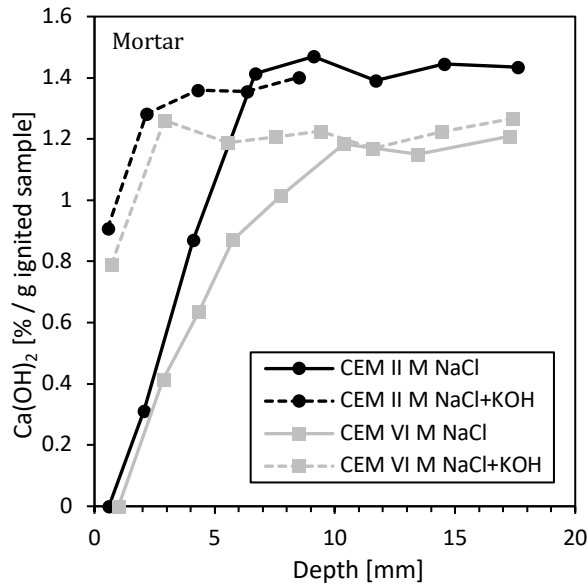


Figure 2 Portlandite ($\text{Ca}(\text{OH})_2$) profiles obtained from TGA for mortar CEM II (black) and CEM IV (grey) samples exposed to 3% NaCl (solid lines) and 3% NaCl+KOH (dashed lines).

3.2 Potassium profiles from ICP-MS

Figure 3 a) shows the potassium (K) profiles of the CEM II mortar and concrete samples exposed to NaCl or NaCl+KOH solution obtained by ICP-MS. Figure 3 b) shows the potassium profiles of the mortar and concrete samples for CEM VI. All samples exposed to a NaCl solution show a clear leaching of potassium towards the exposed surface. Comparing the samples that are exposed to only NaCl, potassium leaching is visible at greater depths in the mortar samples (approx. 10 mm) than in the concrete samples (approx. 5 mm). In the case of the concrete samples, the potassium leaching towards the exposed surface was prevented by the exposure to a NaCl+KOH solution. In the case of the CEM II mortar sample, potassium is still leached out toward the exposed surface, but limited compared to the respective samples exposed to a NaCl solution.

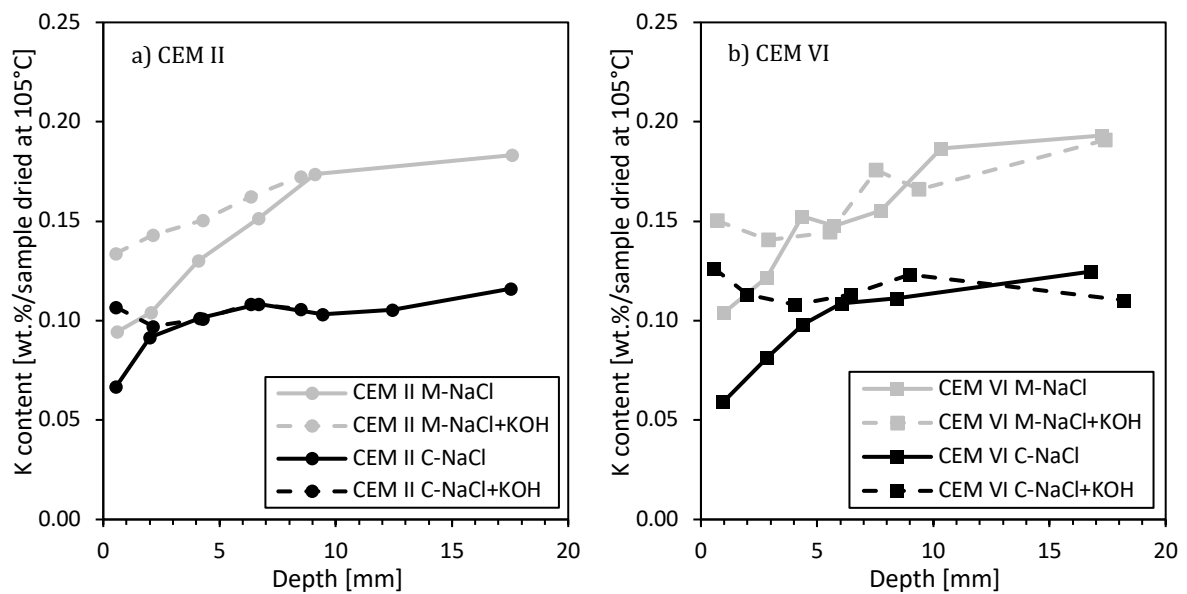


Figure 3 Potassium (K) profiles determined by ICP-MS of a) the mortar (grey) and concrete (black) samples for CEM II (spheres) and b) the mortar and concrete samples for CEM VI (square) after exposure to NaCl (solid lines) and NaCl+KOH (dashed lines) solutions for 90 days.

3.3 Elemental maps from μ XRF scanning

Figure 4 shows the chloride maps for concrete and mortar samples exposed to 3 % NaCl solution (left) and 3 % NaCl+KOH (right) obtained by μ XRF scanning. Sawn blocks from the exposed mortar and concrete samples were analyzed. For the maps in Figure 4 the bottom surface was exposed to the chloride solutions, while the other sides were coated with epoxy. The results presented give a qualitative illustration of the presence of the chloride from the exposed surface inwards. For all samples, the amount of chloride detected in the area close to the exposed surface are much higher in the case of 3% NaCl exposure than in the case of 3% NaCl+KOH exposure. This is slightly less visible for the concrete sample prepared with the CEM VI than in the other samples. The lines of higher chloride contents in the mortar samples are probably surface artefacts, as they superimpose with edges on the discs caused by sawing and polishing with sandpaper. The area of high chloride content in sample CEM II C NaCl+KOH is a chloride-containing aggregate. This was found by comparing the chloride map with the overview picture of the scanned area acquired at the scan. Chloride-containing aggregates, if present, may have an impact on the results for potentiometric titration if the aggregate is dissolved in the acid.

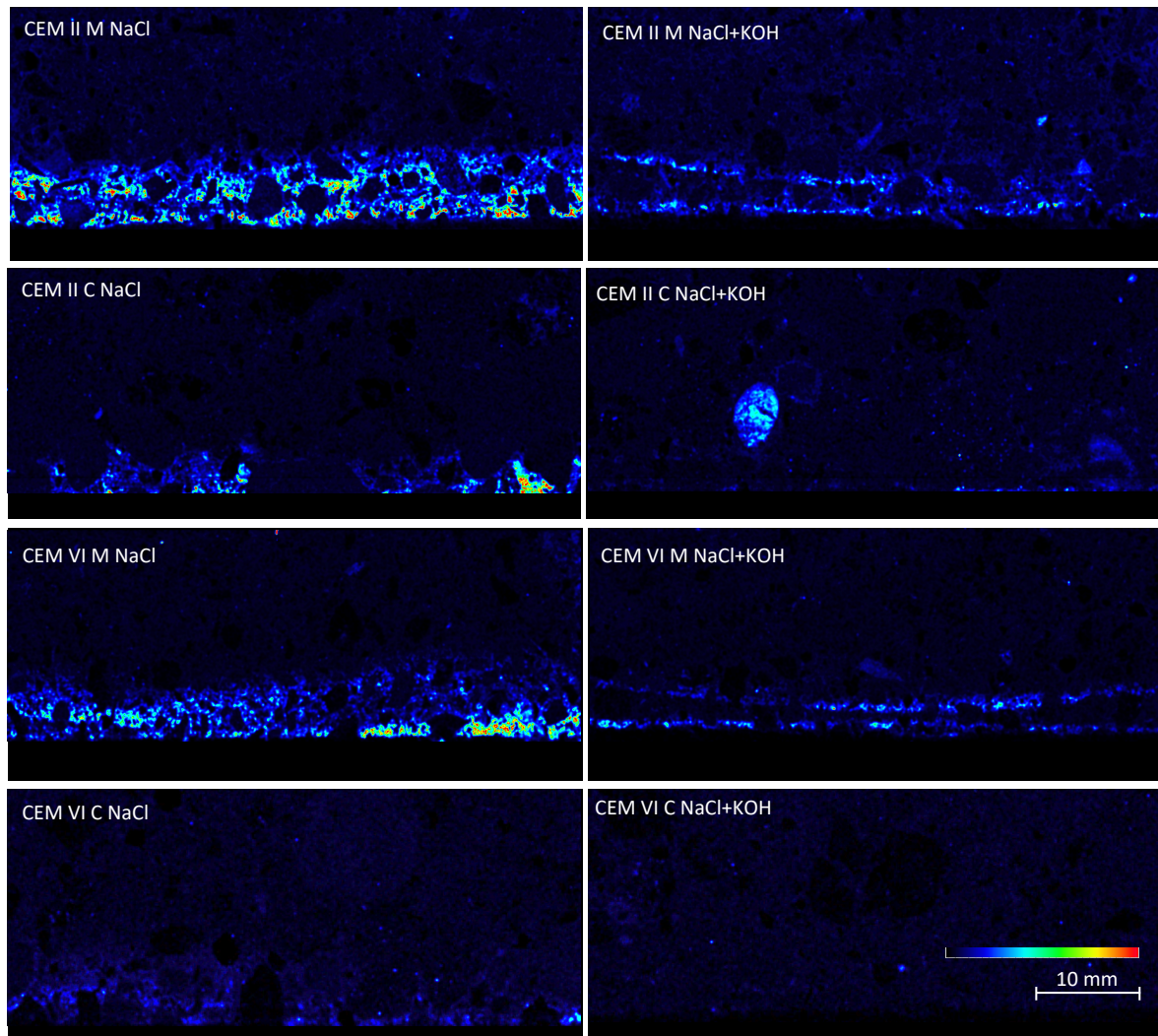


Figure 4 Chloride maps from μ XRF scans for all samples exposed to a 3% NaCl solution (right) or a 3% NaCl+KOH solution (left). The bottom surface was exposed to the chloride solutions in all samples. Dark blue indicates little chloride content, while red indicates high chloride content.

3.4 Chloride profiles

The total chloride contents in all samples determined with potentiometric titration are presented in Figure 5 as a function of the depth from the exposed surface. The points correspond to the center of each profile grinding step. The samples exposed to NaCl solution have a higher chloride content than the corresponding sample exposed to NaCl+KOH solution. In addition, the mortar samples show a higher chloride content than the corresponding concrete for all cases. Taking the background chloride content as a threshold (about 0.02 wt%), the chloride ingress depth is similar for the samples exposed to NaCl or NaCl+KOH solutions.

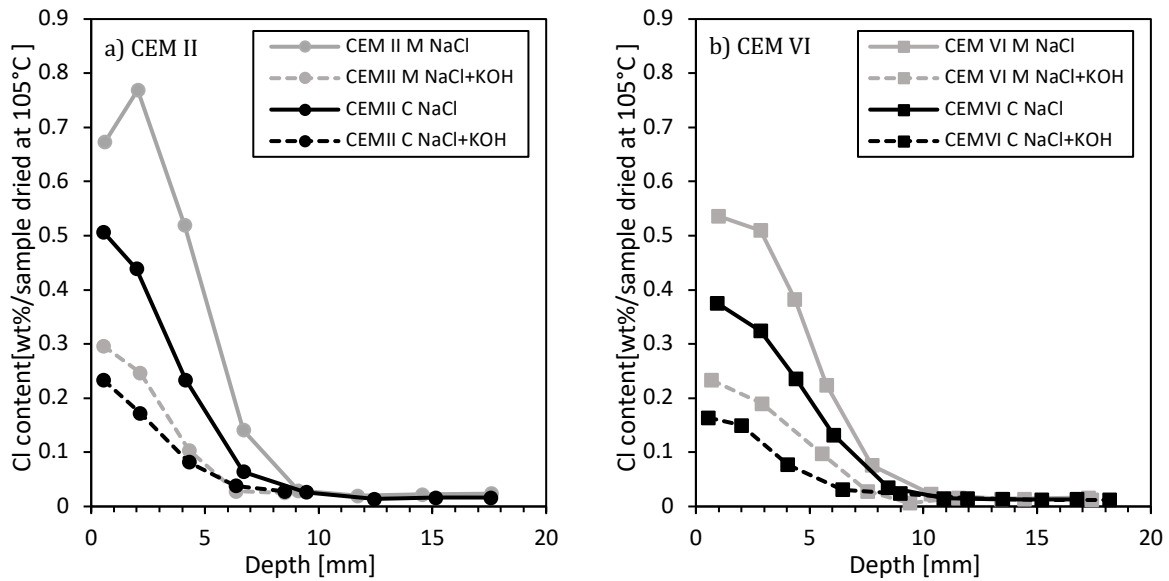


Figure 5 Total chloride content as a function of the depth from the exposed surface for mortar (grey) and concrete (black) samples prepared with the CEM II (a) and CEM VI (b). Samples exposed to NaCl solution are illustrated with solid lines, while samples exposed to NaCl+KOH solution are illustrated with dashed lines.

4. Discussion

4.1 Does leaching affect the chloride profiles in mortar and concrete?

Figure 6 compares the portlandite ($\text{Ca}(\text{OH})_2$) and the chloride profiles. For the samples exposed to NaCl (solid lines), the transitions in the portlandite content and chloride content correspond well with each other. For the samples exposed to NaCl+KOH (dashed lines) the negative correlation is not as clear.

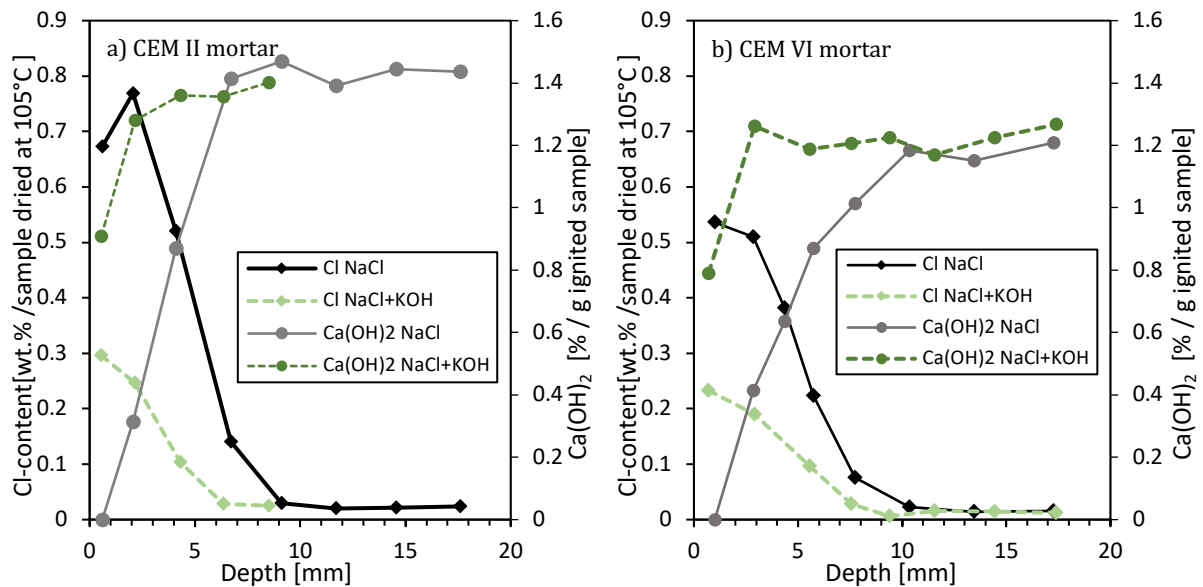


Figure 6 Comparison of chloride content and portlandite ($\text{Ca}(\text{OH})_2$) content in mortar samples exposed to NaCl (solid lines) and NaCl+KOH (dashed lines), for CEM II (a) and CEM VI (b).

In order to facilitate the comparison of the chloride profiles and the portlandite (Ca(OH)_2) profiles, we will compare the depth affected by leaching and by chlorides. The depth affected by leaching is defined as the first point in the portlandite profile where the subsequent point has either the same or a lower portlandite content. The chloride ingress depth is defined as the first point where the Cl-profile flattens out. Figure 7 further compares the chloride ingress depth and the leached depth. The results show that the samples exposed to NaCl (leached) the chloride ingress depth corresponds well with the leached depth. For the samples exposed to NaCl+KOH (limited leaching) the chloride ingress depth is deeper than the leached depth for both binders. The vertical bars in Figure 7 correspond to the length of the profile grinding step and are added to illustrate that the sample is homogenized over a certain depth. When the step size of the profile grinding is considered, the chloride ingress depth and the leached depth are in compliance with each other for all samples, except for the CEM VI mortar sample exposed to NaCl+KOH, where the vertical bars do not overlap. When comparing the chloride ingress depth between the samples exposed to NaCl and NaCl+KOH, the depth does not vary as much as for the leached depth. For CEM VI the chloride ingress depths are comparable with each other when the vertical bars are taken into consideration, while for CEM II they are not. However, they are not considerably different.

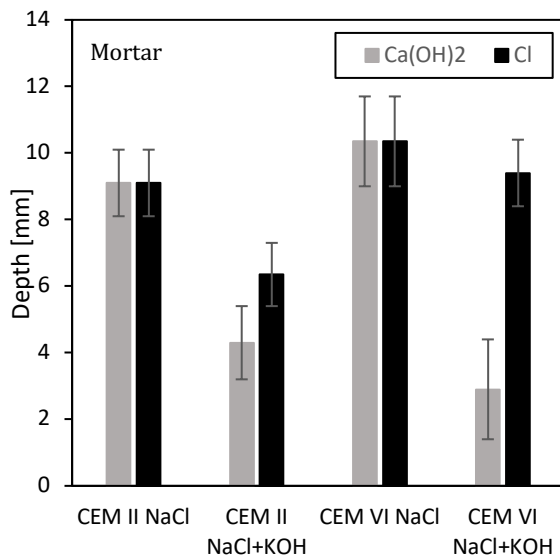


Figure 7 Comparison of leached depth (grey bars) and chloride ingress depth (black bars) in CEM II and CEM VI exposed to NaCl solution and NaCl+KOH solution.

4.2 Shape of chloride profile

Leaching has a significant impact on total chloride content measured in the concrete. Exposure of the samples to a 3% NaCl solution, leads to considerably higher total chloride contents compared to the samples exposed to 3% NaCl+KOH solution, where leaching is limited. For example, the maximum total chloride content in the CEM II mortar is about 0.8 wt% in the heavily leached sample i.e. NaCl exposure, compared to 0.3 wt% when leaching is restricted, i.e. NaCl+KOH exposure (see Figure 5). For CEM VI the respective values are about 0.5 wt% versus 0.2 wt% (see Figure 5). Hence leaching leads to an increase in maximum total chloride content of about 150 %.

The higher chloride content in the more severely leached samples is attributed to an increased binding capacity of the cement paste upon leaching. In a recent study [17,18] we demonstrated that the chloride binding increases when the pH in the exposure solution in equilibrium with the solids is decreased from 13 to 12. The increased binding capacity was attributed to an increased uptake of chlorides by AFm phases as well as adsorption on to the C-S-H. However, in [17,18] we observed that when the pH of the exposure solution in equilibrium with the solids drops below 12, a drastic decrease in the chloride binding capacity of the paste was observed as the hydrates binding the chlorides start to decompose. This could explain the observed reduction in the total chloride content in the outermost section of the CEM II sample exposed to NaCl, as this section does not contain any portlandite anymore and is therefore considered to be leached.

It should be noted that leaching also increases the porosity and permeability of the cement paste and will in this way also affect the chloride ingress and chloride profiles [33]. Upon leaching, the first hydrate to dissolve is portlandite [26,27]. When portlandite dissolves, this consequently leads to an increase in porosity. In the case of the CEM II mortar, which has a portlandite content of 1.4 wt% per ignited sample mass (1.08 wt% per mass at 105 °C), the complete dissolution of the portlandite would lead to an increase in pore volume of 0.45 mL per mass at 105 °C (taking into account portlandite's molar mass of 74 g/mol and molar volume 33 mL/mol). If we assume the worst-case scenario, meaning that this additional porosity is filled with the same chloride concentration as the exposure solution (3% NaCl solution with a density of 1.02 g/mL), this would represent an additional 0.009 wt% chloride per mass of concrete dried at 105 °C. This means an increase in the chloride content in the concrete with 3% compared to the maximum total chloride content measured for the CEM II mortar exposed to NaCl+KOH (see Figure 5). As the difference in total chloride content with and without leaching is about 150%, the difference in total chloride content must be mainly caused by enhanced binding upon progressed leaching.

Based on the obtained chloride profiles it seems that leaching does not considerably affect the chloride ingress depth after 90 days of exposure, as the samples exposed to NaCl have similar ingress depths as the samples exposed to NaCl+KOH (see Figure 7). This indicates that degree of leaching might not affect the chloride ingress depth and thereby also might not affect the service life of the reinforced concrete structure. It should be noted that we would need additional long-term exposure data to be able to conclude on the long-term impact of leaching on the chloride penetration and service life.

However, total chloride content profiles are often used as a basis for empirical service life prediction models. Hence, changes in the total chloride content could lead to large variations in the predicted service life, which on its turn can put to question the validity of these service life prediction models. An example is given in the following section.

4.3 How do the findings impact service life modelling?

We are using the service life prediction model for reinforced concrete structures subjected to chloride induced corrosion described in Chapter 3.2 in Fib bulletin 34 [10]. The approach assumes uncracked concrete. Annex B2 provides an approach to estimate the critical chloride content C_{crit} (wt%/sample dried at 105 °C) at the reinforcement (Equation 3), as well as quantification of the required parameters for the service life calculations. In this case the service life is defined as the time it takes for the chlorides to reach a critical chloride concentration at the steel reinforcement. The approach is based on the error function solution (erf) of Fick's second law of diffusion (Equation 3).

The required parameters to be quantified in Annex B2 in Fib bulletin 34 (2006) and applied to Equation 3 are the following: x is the depth from the exposed surface in (mm), Δx the depth of the convection zone in (mm), a represents the thickness of the concrete cover in (mm), t the time in (years) and $C(x, t)$ the chloride content at depth x and time t in (wt%/sample dried at 105 °C), C_{crit} is the critical chloride content in the concrete, C_0 is the initial chloride content and $C_{S,\Delta x}$ is the chloride content at a depth Δx all in (wt%/sample dried at 105 °C). $D_{app,C}$ is the apparent diffusion coefficient of the concrete in (mm²/year).

$$C_{crit} = C(x = a, t) = C_0 + (C_{S,\Delta x} - C_0) \cdot \left[1 - \operatorname{erf} \frac{a - \Delta x}{2\sqrt{D_{app,C} \cdot t}} \right] \quad (3)$$

In our calculations C_0 was determined by the background chloride content, i.e. the last point in the chloride profiles (approx. 0.02 wt%/sample dried at 105 °C). As we are studying submerged conditions, there is no convection zone, hence Δx is put to 0 mm (2006). As a consequence, $C_{S,\Delta x}$ is equal to the surface chloride content C_s . Hence, the only parameters missing are the apparent diffusion coefficient, $D_{app,C}$, and the surface concentration, C_s .

According to Fib bulletin 34, the D_{app} can be determined based on accelerated laboratory testing, also called the rapid chloride migration tests (RCM). This test has not been performed on the investigated samples. Fib bulletin 34 also proposes that D_{app} and C_s may be estimated from chloride profiles from existing structures, given that the concrete has been exposed for several months. In this example D_{app} and C_s were estimated by fitting Equation 3 by the least mean square method to the chloride profiles presented in Figure 5.

Figure 8 shows the chloride profiles with the fitted curves. Table 3 gives the apparent diffusion coefficient D_{app} and surface chloride content C_s calculated by the fitting of the curves for all mortar samples. The first points in the profiles were not discarded, as the profiles have few datapoints and because of the absence of a convection zone under the submerged conditions.

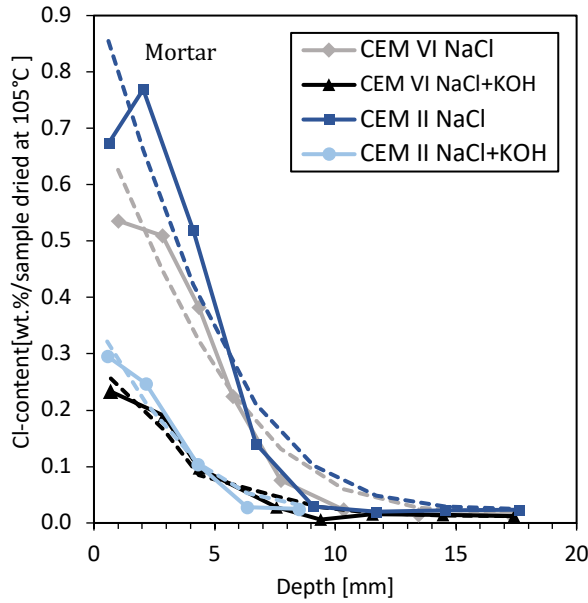


Figure 8 Fitted curves (dashed lines) together with the chloride profiles obtained from titration (solid lines) of all mortar samples: CEM VI samples exposed to NaCl (grey) and NaCl+KOH (black), CEM II exposed to NaCl (dark blue) and NaCl+KOH (light blue).

Table 3 D_{app} , C_0 and C_s , as well as the predicted service life for all mortar samples.

Sample	D_{app} [$10^{-12} \text{ m}^2/\text{s}$] ([mm^2/year])	C_0 [wt%/conc]	C_s [wt%/conc]	Service life [years]
CEM II NaCl	1.8 (56.4)	0.024	0.94	13
CEM II NaCl+KOH	0.9 (27.4)	0.025	0.36	110
CEM VI NaCl	2.0 (62.1)	0.016	0.73	16
CEM VI NaCl+KOH	1.6 (49.9)	0.012	0.29	151

In order to estimate the service life of a structure prepared with the mortars investigated in this study according to the Fib bulletin 34 model, we need to assume a concrete cover, a , and a critical chloride content, C_{crit} . We use the C_{crit} equal to 0.2 wt% as suggested by Fib bulletin 34 (2006) as a lower boundary value for the critical chloride content. The cover depth, a , is determined according to Eurocode 2 section 4 (CEN 2004), where a nominal cover depth of 50 mm is prescribed for the exposure class XS2 (permanently submerged structures exposed to chlorides from seawater). The nominal cover depth consists of a minimum requirement regarding durability $C_{min,dur}$ of 40 mm and a variation ΔC_{dev} of 10 mm.

D_{app} is considered to be time dependent, and by acquiring chloride profiles at different exposure times, one can gain information on the time dependency of $D_{app,C}$. However, in the absence of such information we are using the D_{app} , as well as the C_s , given in Table 3. The service life is calculated as the time to reach the critical chloride content C_{crit} at the reinforcement steel using Equation 3 and the above-named parameters. The results of the service life predictions are also given in Table 3.

The differences in the predicted service life for samples exposed to NaCl solution and NaCl+KOH solution are dramatic. For the CEM VI mortar samples, the one exposed to

NaCl has an estimated service life of 16 years, while the one exposed to NaCl+KOH has an estimated service life of 151 years. For CEM II mortar samples the NaCl exposed sample has a service life of 13 years, and the NaCl+KOH exposed sample has a service life of 110 years. The predicted service life varies with a factor of almost 10 when we compare the leached and less-leached samples. This raises questions regarding the reliability of the applied model and input parameters used. Researchers have been trying to improve similar models by taking into account time dependent surface concentrations and diffusion coefficients.

However, one might question whether models fitting ingress profiles to the total chloride content profiles are a good approach to start with. The total chloride content is merely a reflection of the potential of the solids to take up chlorides and, as demonstrated in this study, is strongly dependent on leaching. One should look at the chloride content as an indicator for how far the chlorides have penetrated the concrete, but not necessarily as a potential for ingress as done by many models. A good illustration for this is that the chloride content at the surface of submerged concrete becomes slightly lower with time than the chloride content a few mm or cm deeper in, also called the peaking-behavior. Hence the total chloride content at the surface cannot be the driving force for the ingress. We should focus on ingress rather than on fitting total chloride content profiles.

This calls for more mechanistic models such as [34,35]. If we want to verify chloride ingress using total chloride content profiles, we need to account for the interactions between the solids and chlorides, their dependency on leaching, binder composition and time.

It also shows that one should take leaching into account when doing performance tests such as [19-23] for chloride ingress as this might strongly influence the chloride profiles. This can be done by having reproducible procedures for the test, e.g. fixed exposed surface vs volume exposure solution ratio, routines for exchanging the exposure solution etc.

5. Conclusions

In order to investigate the effect of leaching on chloride ingress profiles, concrete and mortar cylinders were exposed for 90 days to two different exposure solutions: 3% NaCl, and 3% NaCl with additional KOH to limit leaching. After exposure, total chloride profiles were determined, as well as portlandite and potassium profiles to investigate the extent of leaching.

- The experimental setup with the two exposure solutions achieved different extents of leaching, as shown by the potassium and portlandite profiles.
- Enhanced leaching due to the exposure to 3% NaCl solution leads to higher maximum total chloride contents (+150 %) compared to exposure to 3% NaCl+KOH solution.
- Total chloride content is mainly determined by the interaction between the solids and chlorides, as the increase in porosity due to the leaching of e.g. portlandite

does not explain the big difference in the total chloride content in samples exposed to 3% NaCl and 3% NaCl+KOH.

- The two exposure solutions tested do not affect the chloride ingress depth considerably after exposure for 90 days.
- Leached and less-leached samples show great differences in predicted service life. The changes in total chloride content due to leaching most likely erroneously affect the service life predictions using empirical models. This is another indication that more mechanistic models should be used. Determination of service life should focus more on ingress depth rather than peaks in chloride profiles.
- It is important to take into account leaching when comparing performance test results on concrete for chloride ingress.

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The authors would like to thank the EnDurCrete project partners Rosa Marie Carreras Lample and her colleagues from Acciona for preparing the samples for this study and Aljosa Sajna and his colleagues from ZAG for exposing and preparing profile ground and sawn samples. In addition, we would like to thank Siri Hofstad Trapnes from SINTEF and Tone H. Nilsen from NTNU for the help with the chloride titration, Syverin Lierhagen from NTNU for the ICP-MS analyses, and Petter Hemstad from NTNU for assistance and training in μ XRF.

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2. Ny sement for bedre miljø

Alisa Machner, Marie Bjørndal, Klaartje De Weerd
Byggeindustrien, 2019, (Nr. 16), p. 66

Ny sement for bedre miljø

I EnDurCrete-prosjektet undersøker vi en ny komposittsement; CEM II/C-M (S-LL). Den nye sementen viser at det er mulig å oppnå samme langtidsfasthet som en ren Portlandsement, og samtidig bruke langt mindre klinker og dermed langt lavere CO2 utslipp.

**Alisa Machner,
Marie Helene Bjørndal
og Klaartje De Weerd**
Institutt for konstruksjonsteknikk

Hvorfor fokusere på komposittsementer?

Betong er det mest brukte materialet i verden etter vann. Vi fokuserer på sementen som sammen med vann fungerer som limet i betongen. Det er dessuten sementen som står for hoveddelen av CO2 utslippene relatert til betong. Globalt står sementproduksjonen for 5-8 % av det menneskeskapte CO2-utslippet. Redusering av CO2-utslippet fra sementproduksjon kan derfor gjøre en vesentlig forskjell for klimaregnskapet til byggenæringen.

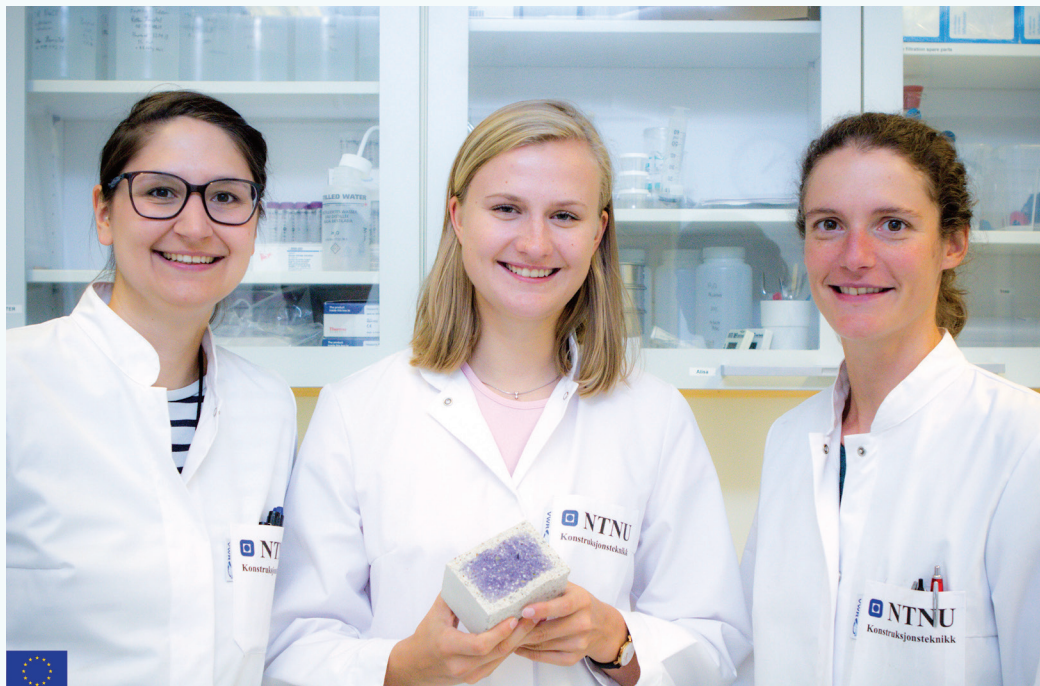
En måte å få ned CO2-utslippene på er å erstatte klinker i sementen med andre tilsetningsmaterialer, som f.eks. slagg, flyveaske eller kalkstein. Slike komposittsementer er derfor betraktelig mere miljøvennlige enn en ren Portlandsement. Spørsmålet er om komposittsementene har like gode egenskaper når det gjelder styrkeutvikling og bestandighet som dagens sementer.

EnDurCrete-prosjektet

EnDurCrete er et EU H2020-prosjekt og står for «ENvironmental friendly and DURable conCRETE» (www.endurcrete.eu), finansiert gjennom EU Programmet Horizon 2020 for Forskning & Innovasjon (prosjektnummer: 760639). Hovedmålet til prosjektet er å utvikle ny kostnadseffektiv og bærekraftig armert betong med lang levetid. Prosjektet er et samarbeid mellom 16 partnere fra 12 land i hele Europa og varer til 2021. NTNU er en sentral partner i prosjektet og forsker på styrkeutviklingen og bestandigheten av betong laget med den nye komposittsementen. Dette innlegget gir noen foreløpige NTNU-resultater før de er behandlet og godkjent av prosjektet.

Ny CEM II/C-M sementen

Sementene vi forsker på innenfor EnDurCrete-prosjektet er nye komposittsementer utviklet av HeidelbergCement som f.eks. CEM II/C-M (S-LL). Denne sementen



NTNU forskerteamet på lab'en. Fra venstre til høyre: Alisa Machner, Marie Helene Bjørndal, Klaartje De Weerd.

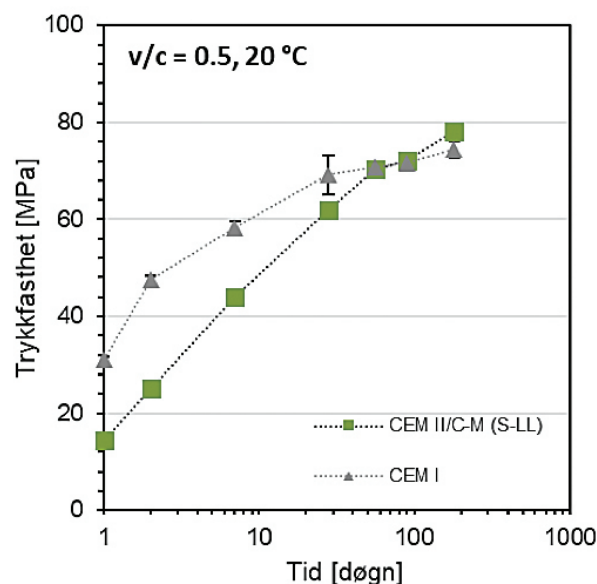
Foto: Andrei Shpak.

tilhører en ny klasse som snart skal finnes i den nye sementstandarden EN 197-1. Den inneholder omkring 50% klinker og resten er forskjellige tilsetningsmaterialer. Siden sementen har en relativt lav klinkerandel, er det viktig at tilsetningsmaterialene reagerer mest mulig. Derfor bruker HeidelbergCement en ny teknologi der alle komponentene av sementen blir malt hver for seg. Slik får vi optimal pakking av partikler og høyest mulig reaksjonsgrad.

Første resultater fra lab'en

Grafen viser at fasthetsutviklingen av den nye komposittsementen (CEM II/C-M (S-LL)) er tregere enn en ren Portlandsement (CEM I med 95 % klinkerandel) første uke etter støpen. Deretter øker fastheten i den nye komposittsementen til samme nivå som referansen. Dette tyder på at tilsetningsmaterialene i sementen bidrar til fastheten over tid.

Forskerteamene ved NTNU, VITO (Belgia) og HeidelbergCement (Tyskland) har undersøkt reaksjonen som fører til fasthetsutviklingen, ved hjelp av avansert teknikk som f.eks. TGA, XRD, SEM og MIP. Resultatene skal brukes til å



Trykkfasthetsutvikling for CEM II/C-M (S-LL) og ren Portlandsement (CEM I)

forklare hvordan komposittsementene herder over tid, avhengig av temperatur eller v/c tall.

Hva skjer videre?

For å utvikle en bærekraftig betong er bestandigheten et viktig tema. Bestandighetsprøving av betong laget med nye komposittsementer er

for øyeblikket i full sving på NTNU, SINTEF, ACCIONA (Spania) og ZAG (Kroatia). Basert på laboratorieresultatene vil vi sammen med eksperter fra CEA (Frankrike) lage modeller som kan forutse den resulterende fasthetsutviklingen og bestandigheten av betong laget med nye komposittsementer.

