



CHANGES IN C-S-H COMPOSITION DURING CHLORIDE EXPOSURE

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ABSTRACT: Mortar samples were exposed to two NaCl solutions with different pH, to investigate the impact of leaching on total chloride profiles. One set of samples was exposed to a NaCl solution, and a set of twin samples was exposed to a NaCl solution additionally containing KOH, to limit leaching. A clear correlation between the leaching depth and the chloride ingress depth was observed. We investigated the changes in the C-S-H composition as a function of the depth from the exposed surface in the two sets of samples with SEM-EDS after 180 days of exposure. The results showed that the Ca/Si ratio of the C-S-H changed only in the outermost 0.7 mm. The Cl/Si ratio of the C-S-H followed the trend observed in the total chloride profiles. The adsorption of sodium and potassium on the C-S-H was also found to be depending on the leaching conditions during the exposure.

1 INTRODUCTION

Chloride induced reinforcement corrosion is one of the major degradation mechanisms for reinforced concrete structures. As basis for the prediction of the (remaining) service life of structures, it is common to determine total chloride profiles, which show the total chloride content in the concrete as a function of the ingress depth. In order to reduce empirical testing and improve the predictions, we need to develop more mechanistic service life models based on the understanding of the interactions between chlorides and concrete.

This abstract presents the findings related to C-S-H composition taken from a study focusing on the interaction of chlorides with the hydration phases in mortar cylinders exposed to NaCl and NaCl+KOH solutions for 180 days [1]. The two exposure solutions enabled the investigation of the impact of leaching on the total chloride profiles. The changes in the C-S-H composition were determined as a function of the depth from the exposed surface using SEM-EDS and were related to the total chloride profiles and CH profiles.

2 MATERIALS AND METHODS

Within this study, mortar cylinders were prepared with a CEM VI (S-V) cement and a w/b ratio of 0.45. The sand (0-4 mm) and cement were mixed in a ratio of 2.7 by mass. In addition, 3.9 kg/m³ admixtures were added to achieve a slump of ≥ 240 mm. The cement used was developed and supplied by HeidelbergCement within the EnDurCrete project framework and consists of 47 wt.% CEM I, 10 wt.% fly ash and 43 wt.% ground granulated blast furnace slag. The preparation of the mortar cylinders (height 200 mm, diameter 100 mm) is described in further detail in [1]. After 76 days of sealed curing, the cylinders were cut to a length of 75 mm, sealed with epoxy (except for the cut surface), pressure saturated and finally exposed for 180 days to two different chloride-containing

solutions (13 mL/cm² exposed surface). A 3 wt.% NaCl solution (acc. to EN 12390-11) was used, as well as a 3 wt.% NaCl solution to which 8.4 g/L KOH was added, in order to limit leaching. The exposure solutions were exchanged weekly. Two twin specimens were exposed to each solution. After 180 days of exposure, one twin test specimen was profile ground from the exposed surface inwards, to obtain powders from various depths. These powders were analysed with thermo-gravimetry to determine their portlandite (CH) content, and dissolved in an HNO₃ solution to determine the total chloride content by potentiometric titration as described in [1]. From the other twin test specimen, a polished section was prepared for SEM-EDS analysis. A Hitachi S-3400N scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) from Oxford Instruments was used, which was operated with an acceleration voltage of 15 keV. Frames at x1.7k magnification at various depths from the exposed surface were investigated at a working distance of 10 mm. In each frame, we collected a minimum of 20 EDS point-analyses of the matrix, representing the intermixed phase assemblage. The results of the EDS point-analyses were used to determine changes in the composition of the C-S-H by plotting the ratios of various elements over an independent element, in this case Mg. The slopes of the resulting linear trend lines allow the determination of elemental ratios i.e. Ca/Si, Cl/Si, Na/Si or K/Si in C-S-H.

3 RESULTS AND DISCUSSION

Figure 1 shows the total chloride profiles, the CH profiles and the elemental ratios of C-S-H determined on samples exposed to the NaCl or NaCl+KOH solution for 180 days as a function of depth from the exposed surface.

For the mortar sample exposed to NaCl, the CH content is reduced in the outer 10 mm, whereas for the NaCl+KOH exposed sample the CH has leached out only in the

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outermost section (0.7 mm). This confirms that we were able to limit leaching with NaCl+KOH compared to the NaCl exposure. Leaching lead to a higher total chloride content, as mortars exposed to NaCl show more than double the total chloride content compared to the mortars exposed to NaCl+KOH at a similar depth. The Cl/Si ratio of the C-S-H increased with increasing total chloride content. Calculations detailed in [1] show that chloride uptake by C-S-H stands for about half of the total chloride content. When comparing the two exposure conditions, the Cl/Si ratio of the C-S-H seems to increase with leaching i.e. the Cl/Si ratio of the C-S-H for NaCl exposure reaches up to 2, whereas upon exposure to NaCl+KOH the Cl/Si ratio stays below 1.

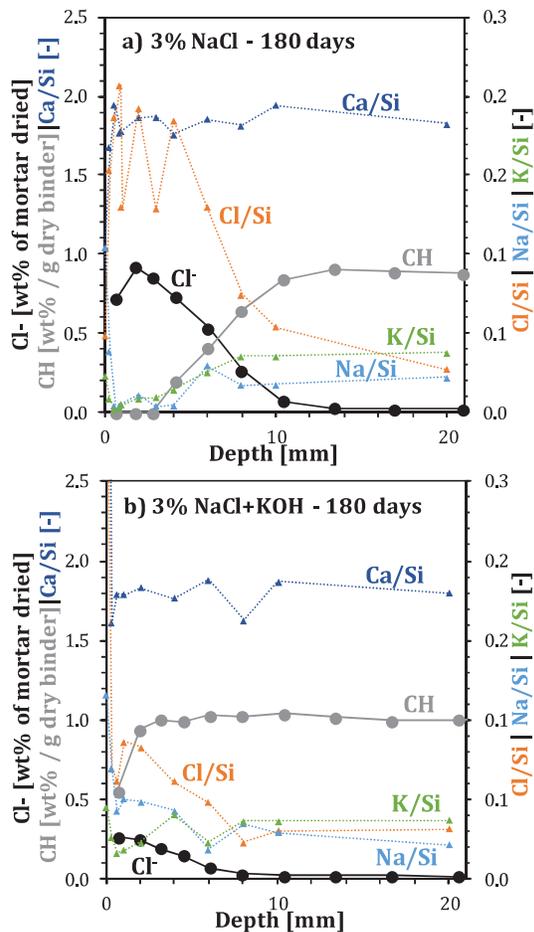


Figure 1: Total chloride and portlandite profiles and elemental ratios determined for C-S-H in the mortar samples after exposure to a) NaCl or b) NaCl+KOH solution for 180 days.

The difference in Cl/Si ratio in the C-S-H as a function of depth or between the two exposure solutions is not caused by changes in the Ca/Si, as the Ca/Si ratio of the C-S-H did not seem to change at depths >0.7 mm. At depths >0.7 mm, the Ca/Si is about 1.8 independent of the depth in both samples, which is assumed to be the Ca/Si ratio of the unaltered C-S-H. A possible explanation for the higher Cl/Si ratio in the case of NaCl exposure might be the

decrease in $[\text{OH}]^-$ ions in the pore solution, due to leaching, which is reducing the competition between chloride and hydroxyl anions for their accumulation in the diffuse layer of the C-S-H [2].

The type of exposure also affects the alkali content in the C-S-H. In the case of the exposure to the NaCl solution, the adsorption of alkalis, such as Na and K, is clearly visible in the outermost section (<0.7 mm) in which the Ca/Si ratio decreased due to leaching. The adsorption of alkalis to de-calcified C-S-H has been reported previously in literature [3]. Slightly deeper into the sample (0.7-4 mm), on the other hand, a clear leaching of alkalis is visible. In the case of exposure to the NaCl+KOH solution, the alkali content only increases towards the exposed surface. This is most likely due to the high pH of the NaCl+KOH solution, which caused the leaching of silicon from this sample, and thereby artificially increased the obtained Na/Si and K/Si ratios in the outermost sections.

4 CONCLUSIONS

The Cl-uptake of C-S-H is estimated to stand for about half of the total chloride content in the mortar. The Cl/Si ratio of the C-S-H increases with leaching. This could not be attributed to changes in the Ca/Si ratio of the C-S-H but might rather be due to the reduced competition with hydroxyl ions due to leaching. The Na/Si and K/Si of the C-S-H increases at the outermost sections due to either decalcification of the C-S-H for NaCl exposure, or Si dissolution in the case of NaCl+KOH exposure.

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