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Impact of the associated cation on chloride binding of Portland cement paste

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ABSTRACT

Well hydrated cement paste was exposed to $MgCl_2$, $CaCl_2$ and NaCl solutions at 20 °C. The chloride binding isotherms for free chloride concentrations ranging up to 1.5 mol/l were determined experimentally. More chlorides were found to be bound when the associated cation was Mg^{2+} or Ca^{2+} compared to Na^+. The chloride binding capacity of the paste appeared to be related to the pH of the exposure solution. In order to explain the cation dependency of the chloride binding a selection of samples was investigated in detail using experimental techniques such as TG, XRD and SEM–EDS to identify the phases binding the chlorides. The experimentally obtained data were compared with the calculations of a thermodynamic model, GEMS. It was concluded that the measured change in chloride binding depending on the cation was mainly governed by the pH of the exposure solution and thereby the binding capacity of the C-S-H.

1. Introduction

Reinforced concrete structures exposed to chlorides from e.g. de-icing salts or sea water have a limited service life due to pitting corrosion of the steel reinforcement. The chlorides propagate through the concrete cover and disrupt locally the protective layer at the surface of the steel reinforcement, causing corrosion of the steel when reaching a critical level.

When a concrete structure is assessed for chloride intrusion generally the total chloride content is determined at varying depths from the exposed surface. Part of the chlorides is bound in reaction products such as Friedel's salts or adsorbed on the calcium silicate hydrates (C-S-H) and part of it is retained in the pore solution. It is the free chloride content, the chlorides retained in the pore solution, which are considered to be the ones able to move and which can cause pitting corrosion of the steel reinforcement. Hence, binding of chlorides in the hydration phases can lower the chloride concentration in the pore solution and reduce the rate of chloride ingress as well as lower the free chloride concentration near the steel.

An understanding of the chloride binding mechanisms is required in order to assess the chloride ingress and the risk of corrosion, thereby potentially improving predictions of the service life of reinforced concrete structures.

2. Background

When studying chloride binding of concrete, cement paste or mortar, chlorides can be introduced internally e.g. by addition to the mixing water or they can be introduced externally by exposing hydrated samples to chloride containing solutions. Internally introduced chlorides affect the hydration of the cement and the microstructure of the hardened cement paste [1].

In this study the focus will be on the exposure to external chlorides meaning exposing hardened cement paste to solutions containing chlorides as this is more representative for chloride ingress in concrete.

Most research on chloride binding of concrete has been done on binding from NaCl solutions [2–7]. This is one of the main de-icing agents used on roads and bridges and the major component of sea water. However $CaCl_2$ and $MgCl_2$ are also used as de-icing agents as they suppress the freezing temperature even more than NaCl, and they are applied as road dust-binders in, for example, tunnels [8]. In addition, Mg and Ca are together with S the major ions present in sea water after Na and Cl. Hence, cations other than Na such as Ca and Mg are of interest when studying chloride binding in concrete.

It has been shown that the cation associated with chloride plays an important role regarding chloride binding [9–13]. Exposure of concrete to $CaCl_2$ solutions has been found to result in more bound chlorides compared to NaCl solutions. $MgCl_2$ behaves similarly as $CaCl_2$ [10,13] as well as HCl [10].

The increased chloride binding for $CaCl_2$ compared with NaCl has been observed to coincide with a decrease in pH in the pore solution [9,12,13]. However the hypotheses for the link between increased

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chloride binding and decrease in pH vary. Tritthart [9] proposed that the observed decrease in the OH^- concentration of the pore solution for $CaCl_2$ and $MgCl_2$ exposure solutions can be attributed to the precipitation of $Ca(OH)_2$ and $Mg(OH)_2$ equivalently with the quantity of the chloride salt added. The inverse relation between the OH^- concentration of the pore water and chloride binding of the cement paste indicates that chlorides are bound through competing adsorption between Cl^- and OH^-, according to Tritthart [9]. Wowra and Setzer [12] proposed that the decrease in the pH is caused by sorption of Ca^{2+} ions on the surface of the C-S-H, rendering the surface positively charged thereby leading to the adsorption of counter ions such as OH^- and Cl^-. Arya et al. [10] and Zhu et al. [13] mention the effect of pH on the solubility of the AFm and AFt phases. Their explanations for the relationship between pH and chloride binding are incomplete and not confirmed experimentally.

The present study is designed to bring the understanding of the impact of the associated cation a step further compared with the abovementioned studies by not only determining the overall chloride binding and in some cases the pH of the exposure solution, but also explaining the cause of these changes. This was done by analysing in a controlled set-up the changes in the elemental composition of the exposure solution and the phase assemblage of a well hydrated cement paste exposed to $MgCl_2$, $CaCl_2$ and NaCl solutions. In addition, the experimental results are compared with the phase changes and changes in the pore solution predicted by a thermodynamic model.

3. Experimental set-up

3.1. Materials

The OPC used in this study was a CEM I 42.5 Portland cement with a Blaine fineness of 573 m^2/kg. The oxide composition of the cement determined by XRF is given in Table 1.

Chloride exposure solutions were prepared with NaCl, $CaCl_2$ and $MgCl_2$. The following three mother solutions were made: 5 M NaCl, 2.5 M $CaCl_2$ and 2.5 M $MgCl_2$. The chloride content of these mother solutions was verified by titration and they were further diluted to solution with the following chloride concentrations: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 M.

3.2. Sample preparation

Cement paste with the CEM I 42.5 and w/c 0.4 was prepared according to [14]. It was cured spread out in sealed plastic bags in a water bath at 5 °C for the first 3 days and at 20 °C for the following 4 days. The resulting cement paste was crushed with a jaw crusher, and subsequently ground to 1 mm fine particles in a rotating disc mill. The resulting powder was stored in 1 l polypropylene bottles with air tight screw caps and an additional 40% of water relative to the powder mass was added to the bottles. The bottles were shaken and the paste was cured at 20 °C for an additional 7 days. The moist hardened cement paste was batch-wise entered into transparent plastic bags, spread on a metal plate, and crushed by a hammer. The resulting samples, looking like “moist sand”, were homogenized and stored air tight in 1 l polypropylene bottles until analysis. This procedure aimed to maximize the degree of hydration of the cement paste and minimize carbonation.

Table 1
Oxide composition of the CEM I 42.5 used in the experiments.

Composition	[%]
SiO_2	19.8
Al_2O_3	5.2
Fe_2O_3	3.5
CaO	61.5
MgO	2.7
SO_3	3.6
K_2O	1.2
Na_2O	0.5
Total Cl	0.056
CO_2	0.35
LOI	1.11
Free lime	1.4

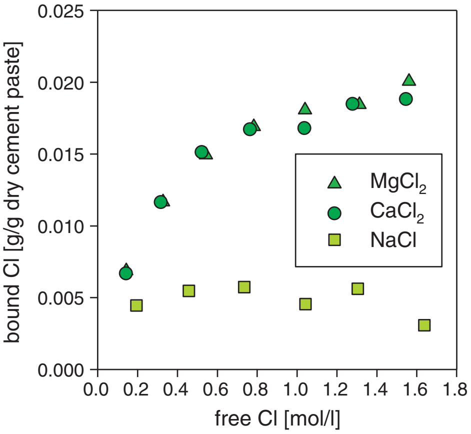

Fig. 1. Chloride binding isotherms for pastes exposed to $MgCl_2$, $CaCl_2$ and NaCl solutions.

The content of free water present in the wet paste and the degree of hydration were determined using TGA. Approx. 400 mg of the wet paste was weighed into a 900 μl alumina crucible and dried in the TGA at 105 °C while purging with N_2 for 4 h at which the weight of the sample had stabilized. The measured weighed loss i.e. the free water content was measured to 59% of the weight at 105 °C. Immediately after, the sample was heated up at a rate of 10 °C/min from 105 to 1000 °C. The measured weight loss in this interval, i.e. the bound water content, was 21% relative to the weight at 1000 °C, indicating a high degree of reaction. The hydrated cement paste had not carbonated during the processes as there was no distinct increase in the weight loss peak detected with the TGA in the carbonate decomposition temperature range (600–800 °C).

For the determination of the chloride binding isotherms, 30 g of the hydrated cement paste (w/c = 0.96) was weighed into 45 ml plastic bottle and 15 ml of the chloride containing solution was added. The samples were shaken regularly and stored at 20 °C for 2 months prior to analysis.

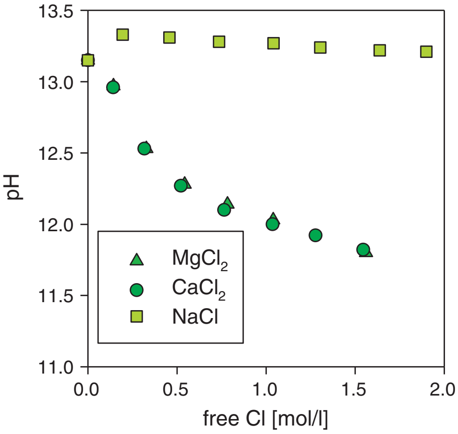

Fig. 2. pH as function of the chloride concentration in the exposure solution for pastes exposed to $MgCl_2$, $CaCl_2$ and NaCl solutions.