Free and bound chloride contents
in cementitious materials

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Abstract
Chloride attack is the main cause of structural damage in reinforced concrete buildings exposed to marine environments. When a certain threshold concentration of chlorides is reached at the concrete-reinforcement interface, the corrosion of the steel rebars is initiated. A part of the intruding chloride ions will be retained by the hydration products of the binder in concrete, either through chemical binding or by physical adsorption. Therefore, chloride binding can delay the achieving of the threshold chloride concentration at the level of the reinforcement by removing chloride ions from the pore solution.

Quantifying the chloride binding process helps predict the service-life of reinforced concrete structures exposed to chloride attack, and allows for a better planning of their maintenance and repair periods. Another important purpose of studying chloride binding is the design of new cement mixes that are able to slow down chloride intrusion, thus improving the durability of future marine structures.

Since the hydration products of cement are responsible for the chloride binding in concrete, this study will focus on the chloride binding in hardened cement paste. A new reaction model will be used in order to predict the hydration products and their relative amounts in an OPC hardened paste. The final scope is to develop an algorithm in order to evaluate the chloride binding capacity of a given cement paste. Two main chloride binding mechanisms – through physical adsorption and through chemical reactions- were taken into account. The model also estimates the amounts of capillary and gel water, thus permitting the calculation of the maximum amount of free chloride ions in the pore solution.

1. Introduction

Chloride attack is the main cause of structural damage in reinforced concrete buildings exposed to marine environments or de-icing salts. The corrosion of the rebars is triggered by the propagation of the chloride ions through the pore solution to the reinforcement level. The intruding chloride ions can be either bound by the hydration products of the binder in concrete, or they can exist as free ions in the pore solution. Therefore, the ability of a concrete structure to resist chloride attack depends among others on its capacity to bind the chloride ions ([1], [2], [3]).

This study deals with NaCl as the source of the intruding chloride ions, for several reasons. The first reason for this choice is that NaCl is the source of chloride ions in marine environments, the most frequent environment for the chloride attack on reinforced concrete structures. Another reason for investigating NaCl as a source of chloride ions is its use in the rapid chloride migration (RCM) test. This widely-used accelerated test for determining chloride ingress into concrete uses a value for the concentration of the external solution of 2 mol NaCl/ L immersion solution ([4]). Therefore, the range of NaCl concentration used in this study is 0-3 M, in order to incorporate all values mentioned above. Ordinary Portland

Cements (OPC) is chosen as binder throughout the study, since it is the simplest system in terms of hydration modeling that still contains all phases involved in chloride binding.

2. OPC hydration products and their interaction with intruding chloride ions

The three main phases (unreacted cement, unreacted water and the hydration products) and the porosity of a hardened cement paste can be studied in terms of mass and volume for a given hydration degree. The hydration degree varies with initial water to cement ratio, age of the cement paste, external conditions for curing and storage etc.

In order to predict the hydration products formed, a new model proposed by Brouwers ([5], [6]) will be used. This model relates the mineral composition of OPC and other important parameters (water to cement ratio, age of the sample, curing conditions etc.) to the amounts of probable hydration products, by studying the reactions that take place upon cement hydration. These calculations are based on a number of limiting conditions regarding the composition of OPC, one of which stipulating that $n_{C3A} > 37/57\ n_{C\bar{S}}$. However, during this study, a number of cement compositions have been found not to follow this condition. For this case, a slightly modified reaction model is being used.

Chloride ions ingressed in the hardened cement paste can be divided into two large groups: free chloride ions, existing in the pore solution, and bound chloride ions, attached to various hydration products. Their sum constitutes the total chloride content of the hardened cement paste. All these concentrations can be related to the concentration of free chlorides in the pore solution, termed "c", and expressed in mol Cl/ liter of pore solution. This method of expression is often employed in literature and also has the advantage of being easily comparable with the chloride concentration of the external environment of the sample.

The two main chloride binding mechanisms – through physical adsorption and through chemical reactions- were considered, along with quantifying the amount of chloride in the pore solution. Out of the considered hydration products in OPC hardened paste, two hydrated phases are known to be able to bind chloride ions- the calcium hydrosilicate (C-S-H) phase ([4], [7], [8]) and the AFm phase ([7], [8], [9], [10], [11]).

Justnes [2] concluded, after an extensive literature review, that chloride binding into cementitious materials is dominated by the content of calcium aluminates and calcium aluminoferrites (by forming Friedel's salt). However, Neville [1] argued that the hypothesis according to which the content of aluminates in cement is proportional to its chloride binding ability is only valid in the case of intermixed chlorides. His study states that the formation of Friedel's salt or chloroferrite from the aluminates takes place rapidly during hydration, while in the case of external chlorides, a smaller amount of chloroaluminates is formed, and that they may become dissociated under certain circumstances, releasing chloride ions so as to replenish those removed from the pore water by transport to the surface of the steel reinforcement.

The C-S-H phase is known to physically bind chloride, due to its high specific surface values. There are several studies about the binding capacity of the C-S-H phase, some of which will be summarized here. Beaudoin et al. [12] have suggested three states of chloride bound to C-S-H: free, adsorbed and interlayer chloride. It is suggested that the chemisorbed and interlayer species can be removed by leaching, while lattice substituted chloride cannot be removed by water. The authors believe that the most of the chloride ions are chemisorbed on the surface of C-S-H and therefore the chloride binding depends on the amount of C-S-H in the sample. Justnes [2] also pointed out the fact that chloride sorption is dominated by the amount of C-S-H.

3. Chloride binding isotherms related to OPC hydration products

Hirao et al. [13] studied the chloride binding of the pure AFm phase. They have found a Freundlich-type isotherm describes chloride binding by the monosulfate phase. Birnin-Yauri and Glasser [10] consider that 100% of the quantity of AFm phase is completely transformed into Friedel's salt at a free chlorides concentration greater than 0.015 mol/L. Both these isotherms are shown in Fig.1 and termed SO_4-AFm and HO-AFm, respectively. Elakneswaran et al. [14] also propose a chloride binding isotherm for the C-S-H phase, which can be fitted to a following Freundlich isotherm. Zibara [8] determined the chloride binding ability on the hydration products of pure C_3S and pure C_2S. Hirao et al. [13] experimentally determined a Langmuir-type isotherm for the chloride binding of the C-S-H phase. A combination of these isotherms that takes into account the C_3S:C_2S ratio of the cement will be used throughout this study.

Using the hydration model described in the previous section, the mass and moles number of each hydrated phase has been estimated for a number of OPC hydrated pastes. The total mass of the hydrated paste has also been estimated, taking into account the relative humidity to which the samples have been conditioned to before the binding experiments. In order to compute the chloride binding capacity of the C-S-H and AFm phases, the amounts of formed C-S-H, C_4ASH_{14} and C_4AH_x have been computed in mg or mmol (m_{CSH} in eq. (1) and respectively $n_{C_4ASH_{14}}$ in eq. (2) and $n_{C_4AH_x}$ in eq. (3)). The total mass of the hydrated paste ($m_{hydrated\ paste}$) has been computed in grams, in order to obtain the results in mg Cl/ g hydrated paste.

In order to combine two C-S-H binding isotherms proposed in [8] into one equation, the mass fractions of C_3S (δ_{C_3S}) and C_2S (δ_{C_2S}) are taken into account in the following relation:

$$C_{b,CSH\ Z} = (6.650\,c^{0.334} \cdot \delta_{C_3S} + 7.888\,c^{0.136} \cdot \delta_{C_2S}) \cdot \frac{m_{CSH}}{m_{hydrated\ paste}} \quad \text{[mg Cl/ g hydrated paste]} \quad (1)$$

The following equations will be used from now on to compute the binding capacities of the two considered AFm phases, obtained from the studies of Hirao et al. [8] and respectively Birnin-Yauri and Glasser [10]:

$$C_{b,C_4ASH_{14}} = 0.8586 \cdot c^{0.5795} \cdot M_{Cl} \cdot \frac{n_{C_4ASH_{14}}}{m_{hydrated\ paste}} \quad \text{[mg Cl/ g hydrated paste]} \quad (2)$$

$$C_{b,C_4AH_x} = 2 \cdot M_{Cl} \cdot \frac{n_{C_4AH_x}}{m_{hydrated\ paste}} \quad \text{[mg Cl/ g hydrated paste]} \quad (3)$$

Fig. 1 shows all the above-mentioned isotherms, describing the chloride binding ability of hydroxy-AFm, monosulfate and respectively C-S-H according to Hirao [13], Zibara [8] and Elakneswaran [14], in mg Cl/ g hydrate, in order to show the considerable difference between them. Fig. 2 shows the same isotherms applied to an OPC hardened paste selected from literature, taking into consideration the relative amount of each hydrate in the cement paste.
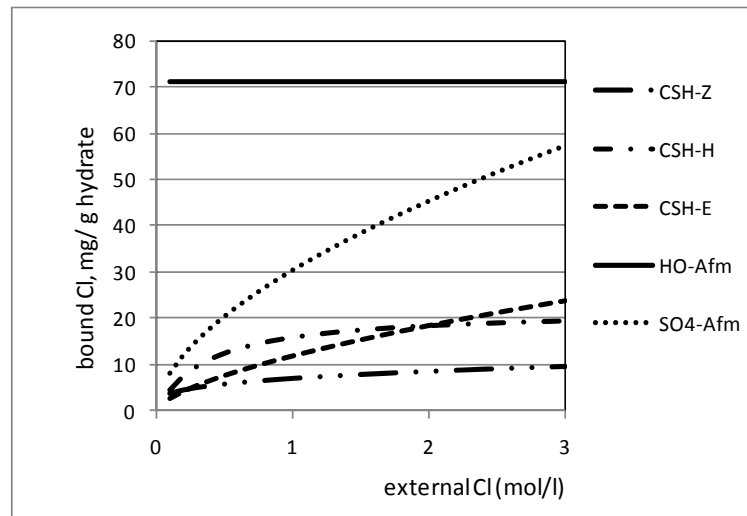
Fig. 1. Isotherms describing the chloride binding ability of hydroxy-AFm, monosulfate and respectively C-S-H according to Hirao, Zibara and Elakneswaran
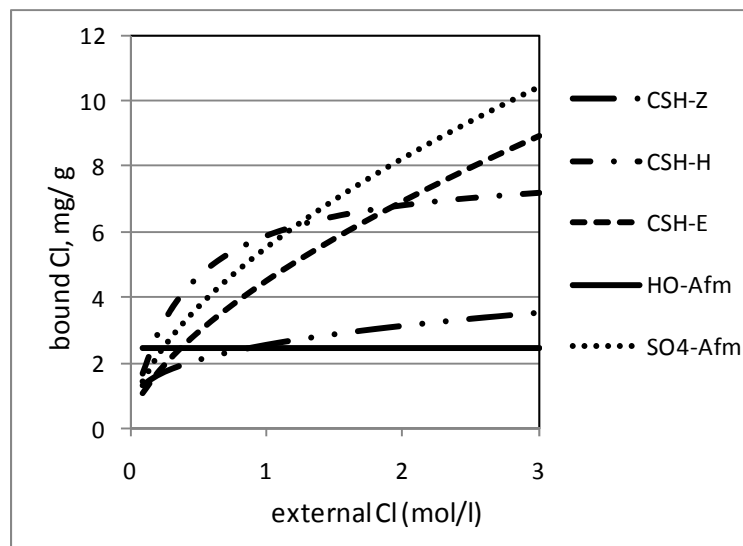

Fig. 2. Pure phases chloride binding isotherms applied to a hardened OPC paste, taking into consideration the relative amount of each hydrate in the cement paste

In order to distinguish between the three mentioned isotherms for the chloride binding of C-S-H, the total bound chlorides will be calculated for a number of hardened cement pastes. The obtained values will be compared to the experimental data and the best C-S-H isotherm will be chosen based on relative error and standard deviation values. Using eq. (2) and (3) for the contribution of the AFm phase and each C-S-H isotherm presented in Fig. 1 and Fig. 2, three isotherms for total bound chlorides will be analysed. These isotherms are termed $C_{b,Z}$, $C_{b,H}$ and $C_{b,E}$ and use the C-S-H binding isotherms proposed in Zibara [8], Hirao [13] and Elakneswaran [14] respectively.

Figure 3 compares these three isotherms with the experimentally determined values for an OPC hardened paste.
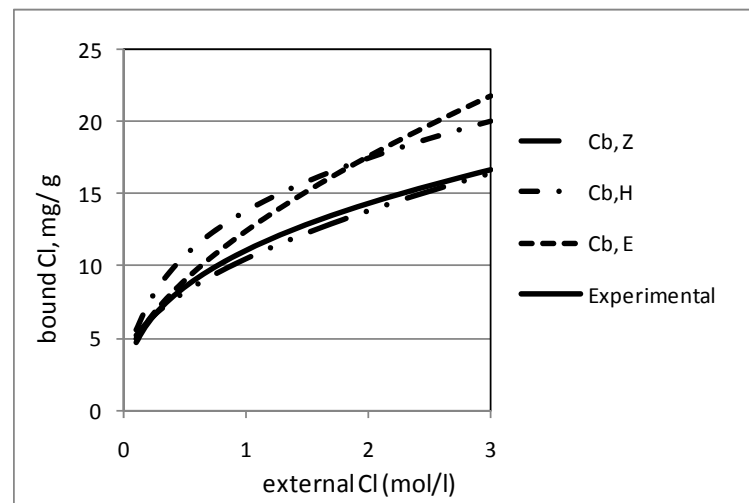
Fig. 3 Comparison between $C_{b, Z}$, $C_{b, H}$ and $C_{b, E}$ and the experimental data for a selected OPC composition.

The best fit was found to be achieved using isotherm $C_{b,Z}$. While the $C_{b,H}$ and $C_{b, \backslash E}$ isotherms have relative errors between 17.1% and 35%, the $C_{b,Z}$ isotherm has relative errors between 3.9% and 10.7%. The standard deviations are also much lower for the $C_{b, Z}$ isotherm (0.48-0.95) when compared to the $C_{b,H}$ and $C_{b,E}$ isotherms. Given these data, the C-S-H-Z isotherm defined as the sum of eq. (1) , (2) and (3) is chosen as the best to describe the chloride binding capacity of the C-S-H phase.

4. Conclusions

New insights into the hydration products of OPC were used in this study. The quantities of hydration products were calculated for saturated state hydration and for samples that have been dried to 11% rh after a certain time of hydration.

Based on an extensive analysis of experimental data found in literature, a new formula for estimating the chloride adsorption capacity of the C-S-H phase is proposed. Using this new formula and several sets of experimental chloride binding isotherms fond in literature, a new chloride binding isotherm for the AFm phase is proposed.

Combining the two new models, for C-S-H and AFm chloride binding in hardened cement paste, and the computed quantities of all hydration products, a new formula for the chloride binding capacity of OPC pastes has been deduced.

When compared to experimental data, the results obtained using the new chloride binding isotherm were excellent. All results are within ±10% of the experimental values for the external concentration range of 0.2 - 3 mol/L.

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