M.V.A. Marinescu; H.J.H. Brouwers

Chloride binding in OPC hydration products

Introduction

Chloride attack is the main cause of structural damage in reinforced concrete buildings exposed to marine environments. The chloride ions, responsible for the initiation of the corrosion mechanism, intrude from the external medium into the concrete. 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. These retained chloride ions are generically referred to as "bound chlorides". Chloride ions that are not bound by hydration products (termed "free chlorides") are able to travel through the pore solution of the binder matrix to the level of the rebars.
When a certain threshold concentration of chlorides is reached at the concrete-reinforcement interface, the corrosion of the steel rebars is initiated. 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 (/1/, /2/). Quantifying this 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. While the aggregates in mortar or concrete can interfere with the transport of the free chlorides, they usually do not affect chloride binding. The structure and the amounts of hydration products that can form in hardened cement paste depend largely on the composition of the cement. Ordinary Portland Cement (OPC) has been chosen as binder throughout this study, since it is the simplest system in terms of hydration modeling that contains all phases involved in chloride binding.
A new model proposed in /3/ and /4/ will be used in order to predict the hydration products and their relative amounts in an OPC hardened paste. This model relates the mineral composition of OPC and other important parameters (water to cement ratio, degree of carbonation etc.) to the amounts of probable hydration products, by studying the reactions that take place upon cement hydration. 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.

Fig.1 shows the mass breakdown between hydrated cement phases in an OPC hardened paste, which will be related to the free and bound chloride amounts. The free chlorides will be found in the pore solution of the hardened cement paste, mainly represented by the unreacted water mass (m_w). The bound chlorides will become a part of the mass of the hydrated cement (m_{hp}).
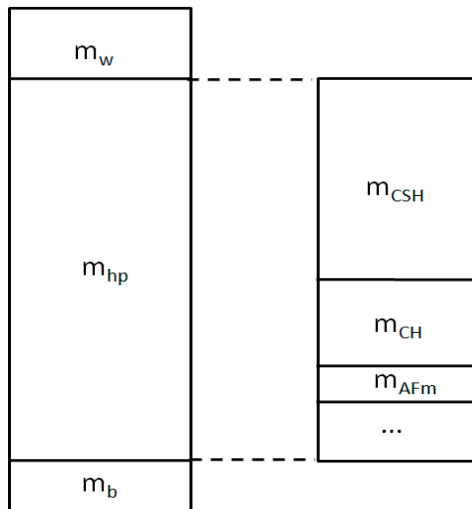
Fig. 1. Breakdown of the cement paste model and the hydration product portioned into the individual hydration products, where m_w = mass of unreacted water, m_b = mass of unreacted binder, m_{hp} = mass of hydration products, m_{CSH} = mass of the CSH phase, m_{CH} = mass of CH, m_{AFm} = mass of AFm phase.

Out of the hydration products of OPC, two phases are known to be able to bind chloride ions: the calcium silicate hydrate (CSH) (/5/, /6/) and the AFm phase (/6/, /7/). The relative amounts of CSH and AFm in OPC hardened cement paste, as derived from /3/ and /4/, are detailed in Fig.1.

Factors that influence chloride binding

The most important parameter that affects the chloride binding capacity of a hardened OPC paste is the composition of the cement. The C_3A content will determine the amount of AFm phase, while the amounts of C_3S and C_2S can be correlated with the amount of CSH formed upon hydration. C_4AF will also play a role, as described in /3,4/. The amount of SO_3 in the cement composition will determine the composition of the AFm phase, as well as the quantity of AFt phase.

Besides cement composition, the next important factor that influences chloride binding is the concentration of free chlorides in the pore solution. The relationship between the concentration of bound chlorides and the concentration of free chloride ions, usually expressed in mol Cl^-/L of pore solution, can be described using chloride binding isotherms. Different types of isotherms have been studied in /5/, with the conclusion that Freundlich isotherms provide the best fit at concentrations of external chlorides greater than 0.01 mol NaCl/L solution, which is the case in marine environments. The typical concentration of NaCl in seawater is fairly constant, ranging between 0.6-0.7 mol NaCl/L. In salty lakes, the NaCl concentration can even reach 3 mol/L.

Other factors that influence the chloride binding capacity of hardened cement paste are the water-to-cement ratio, temperature, degree of carbonation, pH of the pore solution (/1/). An increased water-to-cement ratio leads to increased chloride binding, partly because it promotes a higher hydration degree and partly because it leads to a higher porosity of the hardened cement paste, thus facilitating the transport of free chlorides through the structure. A higher temperature seems to increase chloride binding from concentrated solutions (around 3 mol NaCl/L), but it can decrease chloride binding when the free chlorides concentration is under 1 mol NaCl/ L (/1/, /6/). An increase of

the degree of carbonation of the paste will decrease the chloride binding in a hardened OPC paste (/1/, /6/). The same effect is observed in the case of an increase of the pH of the pore solution. While the cement composition and water-to-cement ratio can be controlled, the external temperature and carbonation of a structure can only be measured and their effects quantified and predicted.

Chloride binding mechanisms

With regard to the two hydrated phases that can bind chlorides (CSH and AFm), both main chloride binding mechanisms (through physical adsorption and through chemical reactions) will be considered. There are several studies concerning the capacity of the CSH phase to physically bind chlorides (/2/, /8/). In /8/, three states of chlorides are identified: free, adsorbed and interlayer chloride. It is suggested that the adsorbed and interlayer species can be removed by water, while lattice-substituted chlorides cannot be removed by leaching. It is concluded that most of the chloride ions are chemisorbed on the surface of CSH and therefore the chloride binding depends on the amount of CSH in the sample. In /2/ it is also indicated that chloride sorption is dominated by the amount of CSH.

In order to explain the capacity of the CSH phase to physically bind chlorides, the electrical double layer theory has been considered (/6/). According to this model, the chloride binding capacity of the CSH phase depends on a number of parameters, such as: the specific surface of the CSH gel, temperature, concentrations of various ions in the pore solution and their respective electrical charge.

The AFm phase is known to bind chlorides through a chemical reaction, with the formation of Friedel's salt /1-2, 7-9/. There are two different mechanisms proposed in literature for this transformation (/1/). The first one is the ion exchange mechanism, which implies that chloride ions are bound by replacing hydroxyl ions from the interlayers of the hydroxy-AFm phase. The second mechanism is based on the fact that the AFm phases have layered structures derived from the structure of portlandite, by the ordered replacement of one Ca^{2+} ion out of three in a $Ca(OH)_2$ layer by an Al^{3+} ion. This substitution causes a charge imbalance in each principal layer, which is corrected by the adsorption of a Cl^- ion in the interlayer space.

Quantifying the chloride binding capacities of OPC hydration products

All experimental results selected from literature and that are used in this study were obtained using the "equilibrium method". This technique implies the immersion of small pieces obtained by crushing the concrete sample in a chloride solution of known concentration, in a sealed environment, until equilibrium is reached. It was concluded in /5/ that a equilibrium between the concentration of free chlorides in the pore solution and the chloride concentration of the external solution is reached within two weeks. Due to the small dimension of the sample pieces, the concentration of chloride ions in the pore solution is considered to be equal to the concentration of the external solution at the time of equilibrium.

In /6/, the chloride binding ability of the hydration products of pure C_3S and pure C_2S, (termed C_3S Z and respectively C_2S Z in Fig. 2.) were determined. Using the model

described in /3/, the amounts of CSH and CH were computed for these two paste compositions. The results in /6/ are, in this way, related to the amount of CSH formed before the immersion of the crushed samples in the chloride solution.

Fig.2. compares the chloride binding isotherms of C_3S and C_2S as found in /6/. The "CSH" isotherm is computed using the C_3S/C_2S ratio on an arbitrary OPC composition selected from /6/, in order to calculate the average chloride binding capacity of the CSH phase. Due to the fact that usually C_3S will be found in a greater proportion in OPC than C_2S, the "CSH" line is closer to the chloride binding isotherm of the C_3S paste.
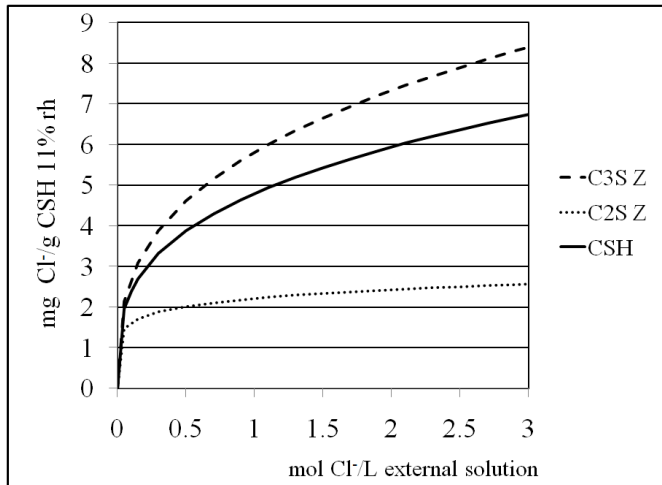

Fig. 2. Chloride binding isotherms of the CSH phase in the hardened cement paste, from /6/. All results represent mg of bound Cl^-/g of CSH dried at 11% rh.

Quantifying the amount of chlorides bound by the AFm phase has to take into account the different types of AFm that can co-exist in hardened cement paste (monosulfoaluminate, hydroxy-AFm, monocarboaluminate or hemicarboaluminate etc.) and also the extent of their solid solutions between themselves and with Friedel's salt. Most experimental data available in literature does not take into account the possibility of carbonation or does not mention the extent of it. The same is true for the distinction between the hydroxy-AFm and monosulfoaluminate (with the exception of /7/, where pure hydroxy-Afm was studied).

Using the model presented in /3/, the composition of the AFm phase can be estimated from the experimental data available in literature.
In /9/, the chloride binding capacity of a C_3A-gypsum hydrated paste was fitted on a Freundlich isotherm, with a maximum at around 3 mol NaCl/L solution. In /7/, the hydroxy-AFm phase is considered to be completely converted to Friedel's salt at a very low concentration of free chlorides, around 0.015 mol NaCl/L solution. No studies regarding the chloride binding capacity of monocarboaluminate or hemicarboaluminate were found for this comparison.

Fig. 3. compares the Freundlich isotherm from /9/, which is attributed here to monosulfoaluminate-AFm, to an isotherm based on the results in /7/ about hydroxy-AFm chloride binding.No mention on the possibility of carbonation was found in /7/ or /9/, so the formation of hemicarboaluminate or a solid solution could not be assumed.
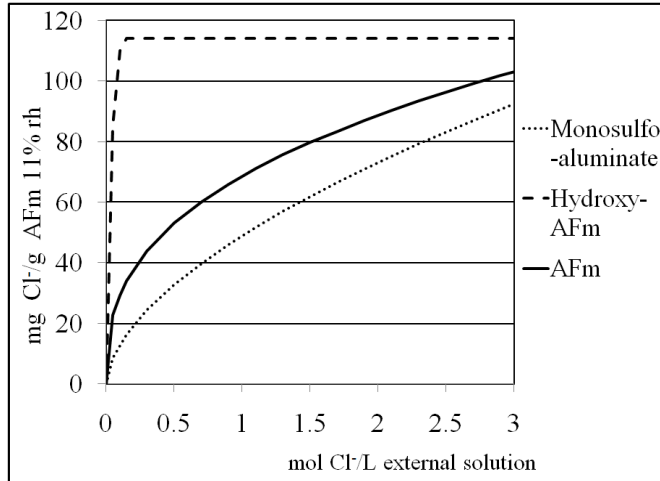
Fig. 3. Chloride binding isotherms of the AFm component in the hardened cement paste, from /7/ and /9/.

The "AFm" isotherm represents a probable chloride binding isotherm of the AFm phase in OPC, fitted on a whole range of OPC compositions and hardened OPC phase parameters found in literature (/5/, /6/). In order to relate this isotherm to the hardened cement paste composition, the reactions between other AFm phases and chloride ions have to be taken into account, as well as the extent of the solid solutions that Friedel's salt can form. Another factor that could influence the experimental results can be the hydration of unreacted cement particles in the chloride-containing pore solution, in the case of cement pastes cured for a short time before immersion into chloride solutions.

Conclusions

Fig. 4. shows the breakdown of bound chlorides in an OPC paste, between the AFm and the CSH phases. The chloride binding capacity is expressed for an arbitrary OPC composition from /6/, in mg Cl⁻/g reacted cement.
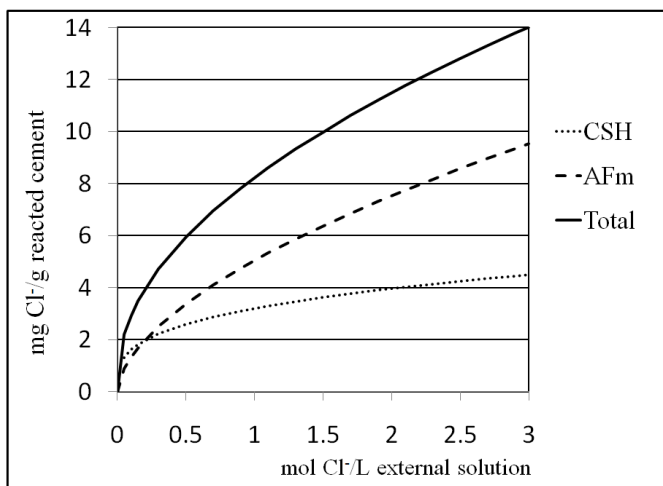

Fig. 4. Bound chloride isotherm as the sum of the binding isotherm of the AFm and the binding isotherm of the CSH phase.

The "Total" line represents the sum of the "AFm" and "CSH" isotherms (computed the same way as in Fig. 2. and Fig. 3.), and is lower than an experimental OPC chloride bonding isotherm of the same OPC hardened paste.

The fact that both the CSH binding capacity and the total binding capacity of hardened OPC pastes can be described using Freundlich adsorption curves suggests that the AFm chloride binding capacity should follow the same trend. This trend, also observed experimentally, leads to the conclusion that the chloride ions adsorption mechanism is the dominant one for AFm chloride binding.

It can be seen in Fig. 4. that the CSH phase accounts for approximately one third of the total bound chloride. However, with the development of the model to include other AFm phases and further approach experimental values, its contribution is expected to be found slightly lower. Further studies of the chloride binding capacity of different AFm phases are needed in order to bring the predicted values closer to the experimental ones. Still, the role of the adsorbtion of chloride ions on the CSH surface can not be neglected when considering the total binding capacity of hardened OPC pastes.

References

/1/   Qiang Yuan et al. (2009), "Chloride binding of cement-based materials subjected to external chloride environment – A review", Construction and Building Materials 23, Issue 1, pp. 1-13

/2/   Justnes, H. (1996), "A Review of Chloride Binding in Cementitious Systems, Cement and concrete", Trondheim, Norway

/3/   H.J.H. Brouwers (2004), "The work of Powers and Brownyard revisited: Part 1", Cem Concr Res 34, 1697-1716

/4/   H.J.H. Brouwers (2005), "The work of Powers and Brownyard revisited: Part 2", Cem Concr Res 35, 1922-1936

/5/   Tang, L. and Nilsson, L.-O. (1993): "Chloride Binding Capacity and Binding Isotherms of OPC Pastes and Mortars", Cem. Concr. Res., Vol. 23 pp. 247-253

/6/   Zibara Hassan, (2001) "Binding of external chloride by cement pastes", PhD thesis, Department of Building Materials, University of Toronto, Canada

/7/   Birnin-Yauri, U.A. and Glasser, F.P. (1998), "Friedel's salt, $Ca_2Al(OH)_6(Cl,OH).2H_2O$: its solid solutions and their role in chloride binding", Cem. And Concr. Res., Vol.28, No.12, pp.1713-1723

/8/   Beaudoin, J.J., Ramachandran, V.S. and Feldman, R.F. (1990), "Interaction of chloride and C–S–H", Cem Concr Res 20 (6), pp. 875–883

/9/   H.Hirao, K.Yamada, H.Takahashi, H.Zibara (2005), "Chloride binding of cement estimated by binding isotherms of hydrates", Journal of Advanced Concrete Technology, Vol.3, No.1, 77-84

Authors:

Dipl. Eng. M. Marinescu
Eindhoven University of Technology
Department of Architecture,
Building and Planning
P.O. Box 513
NL ─ 5600 MB Eindhoven

Prof. dr. ir. H.J.H. Brouwers
Eindhoven University of Technology
Department of Architecture,
Building and Planning
P.O. Box 513
NL ─ 5600 MB Eindhoven