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Modelling of chloride binding related to hydration products in slag-blended cements

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HIGHLIGHTS

- The composition of the slag is crucial to the chloride binding capacity of a paste.
- The interaction between the slag and OPC components is taken into account.
- The C–S–A–H phase binds approximately two thirds of the total bound chlorides.
- The remaining third is attributed to AFm phases.
- The results of the model are highly improved from a previous model from literature.

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ABSTRACT

An improved hydration model of slag-blended cements, taking into account new insights, is used to estimate and quantify the hydration products of slag-blended cements. Individual chloride binding isotherms are used to correlate these amounts of hydration products with the amount of bound chlorides. A number of parameters are directly or indirectly taken into account when estimating the chloride binding ability of a slag-blended cement paste: cement composition, slag content, water/binder ratio, curing age, and free chloride concentration. The model allows the study of the breakdown of bound chlorides by hydration products and their source – either the OPC or the slag.

1. Introduction

The durability of concrete structures in marine environments is strongly related to their deterioration under chloride attack. 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 [1]. 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 [2,3]. Quantifying this process helps to more accurately 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.

The source of chlorides in this study is considered to be NaCl, as explained in [1]. The typical concentration of NaCl in seawater is fairly constant, ranging between 0.6 and 0.7 mol Cl^-/l (M) seawater. In the case of salty lakes, the chloride concentration can reach over 3 M. A widely-used accelerated test for determining chloride ingress into concrete, the Rapid Chloride Migration (RCM) test, uses a value for the concentration of the external solution of

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~1.8 mol NaCl/l (1.83 M) immersion solution [4]. Therefore, the range of NaCl concentration used in this study is 0–3 M, the same as employed in [1].

A number of studies have considered the ability of slag-blended cements to resist chloride attack [2,5–8]. A consensus exists upon the increased capacity of slag blended cements to bind chlorides, compared to pure OPC. This phenomenon has been attributed to the higher alumina content of slag [7], or to the $[OH^-]/[Cl^-]$ ratio [5] and the negative role of sulphates has been highlighted [9]. In this study, only data obtained by the intrusion of external chloride ions into the sample [6] were employed, as opposed to internally-mixed chlorides [5,8]. Also of importance was the determination of complete chloride binding isotherms [6] as opposed to the chloride binding in one specific external chloride concentration point [5,8] and the availability of the compositional data regarding the OPC and slag employed [7]. All data employed in this study regarding chloride binding (selected from [6]) has been obtained using the "equilibrium method", in which the crushed hardened sample is kept in a NaCl solution of known concentration until equilibrium is reached.

In order to relate the amount of bound chlorides to the individual chloride binding capacity of each hydrated phase, a hydration model for slag-blended cements was needed. For this purpose, a combination of the OPC hydration model employed [1], based on the work of Brouwers [10–12], the slag-blended cement hydration model by [13,14] and newer findings from literature [15–18] are used.

The binding ability of slag-blended cements comes from the interaction between the hydration of the cement and that of the slag. The two components react with different rates, and the slag hydration is activated by the portlandite formed during the OPC hydration. The two separate hydration processes lead to the formation of hydration products, some of which can be traced back to the reaction of OPC components, some to the reaction of slag with water and portlandite, and some which are common to both processes. Here, the hydration of the OPC-component and the slag one will also be considered separately for the modelling point of view, even though the consumption of portlandite is not their only interaction in real OPC–slag systems (as detailed in Section 2).

2. The paste model

2.1. The hydration of the OPC component

As described in [1], the hydration of OPC is modelled based on a study of Brouwers [10–12] and takes into consideration the particular case of no carbonation. Table 1 reviews the chemical equations that describe the hydration of OPC under water-saturated conditions, while Table 2 details the molar equations used to compute the amounts of formed hydration products. The same notations used in [1] were kept, with the exception of the superscript OPC, used to differentiate these hydration products from the ones of the slag component.

Table 1
The chemical equations describing the formation of saturated (100% r.h.) hydration products from slag-blended cements [10–12].

$C_3S + 4.5H \rightarrow C_{1.7}SH_{3.2} + 1.3CH$	(1.1)
$C_2S + 3.5H \rightarrow C_{1.7}SH_{3.2} + 0.3CH$	(1.2)
$C_3A + C\bar{S} + 14H \rightarrow C_4A\bar{S}H_{14}$	(1.3)
$C_3A + CH + 21H \rightarrow C_4AH_{22}$	(1.4)
$C_3A + 3C\bar{S} + 36H \rightarrow C_6A\bar{S}_3H_{36}$	(1.5)
$C_4AF + 2C_3S + 22H \rightarrow C_6AFS_2H_{18} + 4CH$	(1.6)
$C_4AF + 2C_2S + 20H \rightarrow C_6AFS_2H_{18} + 2CH$	(1.7)
$C_{n_C^{sl}}S_{n_S^{sl}}A_{n_A^{sl}}M_{n_M^{sl}}\bar{S}_{n_{\bar{S}}^{sl}}F_{n_F^{sl}} + n_H H + n_{CH} \rightarrow n_{C-S-H}^{sl}C_aSA_bH_{(a+1.5)} + n_{HT}^{sl}M_5AH_{13} + n_{HG}^{sl}C_6AFS_2H_8 + n_{AFt}^{sl}C_6A\bar{S}_3H_{32} + n_{HO-AFm}^{sl}C_4AH_{13}$	(1.8)

Table 2
Molar relations between the amounts of hydration products and the mineral composition of OPC [10–12], as described in Section 2.1.

$n_{C_4A\bar{S}H_{14}}^{OPC} = \alpha \cdot 0.5n_{C\bar{S}}$	(2.1)
$n_{C_4AH_{22}}^{OPC} = \alpha(n_{C_3A} - 0.5n_{C\bar{S}})$	(2.2)
$n_{C_6A\bar{S}_3H_{36}}^{OPC} = \alpha \cdot 0.25n_{C\bar{S}}$	(2.3)
$n_{C_{1.7}SH_{3.2}}^{OPC} = \alpha(n_{C_3S} + n_{C_2S} - 2n_{C_4AF})$	(2.4)
$n_{C_6AFS_2H_{18}}^{OPC} = \alpha \cdot n_{C_4AF}$	(2.5)
$n_{CH}^{OPC} = \alpha(1.3n_{C_3S} + 0.3n_{C_2S} - n_{C_3A} + 1.4n_{C_4AF} + 0.5n_{C\bar{S}})$	(2.6)

As this OPC hydration model is extensively described in [3,10–12], no further details will be given here. One observation should be made, however, on the composition of C–S–H, which will be relevant further. A number of studies [15,19,20] have reported a C/S ratio of 1.8–1.85 for pure C–S–H in OPC pastes, together with a substitution of the Si by Al. The A/S ratio in OPC C–S–H was found to be roughly 0.08 [15,19]. These values would lead to a C/(S + A) value of 1.7, which is consistent with [1]. However, the initial OPC hydration model does not take into account the Al substitution into C–S–H, but considers C/S to be 1.7. Hence, the C–S–H structure $C_{1.7}SH_{3.2}$, used so far to describe composition of this hydration product, will be also considered in this article for the hydration of OPC. This choice will be described also from the chloride binding point of view in Section 4.2. In the case of slag-blended paste, the notation "C–S–A–H" will be used to describe the calcium aluminosilicate hydrate phase, which is known to be able to incorporate higher alumina amounts [15,18–20].

An important point is the way the mass of sample will be calculated throughout this study. There are three types of samples which will be considered: pure OPC hydrated pastes, termed HCP1–HCP3 for "hardened cement paste", OPC–slag blended hydrated pastes, termed S1–S5 and theoretically computed "slag only" in which only the hydration products formed with the aid of CH (which is generated by hydrated OPC) are considered to constitute the sample (further details in Section 5). Moreover, the masses of all these samples will be computed at 11% r.h. The experimental data concerning the chloride binding capacity of hardened pastes employed in this study [6] are also based on samples dried at 11% r.h. The water loss of certain hydration products upon drying has been estimated in [10–12,21]. This phenomenon leads to a decrease of molecular mass of the hydration products; however, the molar quantities are unaffected.

Using the molar amounts computed using the equations in Tables 2–4, and the molecular masses of all considered hydration products at 100% r.h. and 11% r.h. (Table 5), the mass of each hydrated product at either of the two relative humidities considered can be computed:

$$\begin{aligned} m_{C_{1.7}SH_{2.1}}^{OPC} &= n_{C_{1.7}SH_{3.2}}^{OPC} M_{C_{1.7}SH_{2.1}}; \\ m_{C_aSA_bH_{(a+0.5)}}^{sl} &= n_{C_aSA_bH_{(a+1.5)}}^{sl} M_{C_aSA_bH_{(a+0.5)}}; \\ m_{C_{\bar{a}}SA_bH_{(\bar{a}+0.5)}}^{total} &= n_{C_{\bar{a}}SA_bH_{(\bar{a}+1.5)}}^{total} M_{C_{\bar{a}}SA_bH_{(\bar{a}+0.5)}}, \quad \text{etc..} \end{aligned} \tag{1}$$

Table 2 lists the way all OPC hydration products molar amounts ($n_{C_{1.7}SH_{3.2}}^{OPC}$, $n_{C_6A\bar{S}_3H_{12}}^{OPC}$, etc., Eqs. (2.1)–(2.6)) that can be computed from the initial OPC composition.

Therefore, the total sample mass in the case of OPC hydrated pastes (HCP1–HCP3) will be computed as follows:

$$\begin{aligned} m_{spl}^{OPC} = {} & m_{C_{1.7}SH_{2.1}}^{OPC} + m_{C_4A\bar{S}H_{10}}^{OPC} + m_{C_6AFS_2H_8}^{OPC} + m_{C_6A\bar{S}_3H_{12}}^{OPC} + m_{C_4AH_{13}}^{OPC} \\ & + m_{CH}^{OPC} + (1-\alpha)\left(b_0^{OPC} - m_{UO}^{OPC}\right) + m_{UO}^{OPC} \end{aligned} \tag{2}$$