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.

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.

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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...
used to differentiate these hydration products from the ones of the slag component.

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 C1.7SH3.2, 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 alumino-silicate 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:

\[
\begin{align*}
\text{mass}_{\text{OPC}} & = m_{\text{OPC}}, \\
\text{mass}_{\text{S1}} & = m_{\text{S1}}, \\
\text{mass}_{\text{S5}} & = m_{\text{S5}}, \\
\text{mass}_{\text{total}} & = m_{\text{total}},
\end{align*}
\]

Table 2 lists the way all OPC hydration products molar amounts \(n_{\text{OPC}}, n_{\text{CAS}}, n_{\text{CASH}}, \text{etc.} \) 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:

\[
m_{\text{sample}} = m_{\text{HCP1}} + m_{\text{HCP2}} + m_{\text{HCP3}} + m_{\text{S1}} + m_{\text{S2}} + m_{\text{S3}} + m_{\text{S4}} + m_{\text{S5}}.
\]
Table 3
Molar relations between the amounts of hydration products and the oxide composition of slag in slag-blended cements [13,14], as described in Section 2.2.

\[
\begin{align*}
\text{MOH}_{\text{sl}} &= \text{MOH}_{\text{sl}} + \gamma \left[ n_2 + n_{\text{MOH}_{\text{sl}}} \right] - \gamma \cdot n_2^2 \\
\text{MOSH}_4_{\text{sl}} &= \gamma \cdot n_1^2 \\
\text{MOS}_{\text{sl}} &= \gamma \cdot n_1 \\
\text{MOS}_{\text{sl}} &= \gamma \cdot n_2 \\
\text{MOSH}_4_{\text{sl}} &= \text{MOH}_{\text{sl}} + \frac{b}{c} \quad \text{in CaSAl}_{4}H_{1+5} \\
\end{align*}
\]

Table 4
Final molar amounts of hydration products in slag-blended cements after the hydration of both the OPC and the slag component, as described in Section 2.3.

<table>
<thead>
<tr>
<th>Formula and molecular mass</th>
<th>OPC</th>
<th>Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6A</td>
<td>645.50</td>
<td>M5AH7</td>
</tr>
<tr>
<td>C6AFS2H18</td>
<td>1042.67</td>
<td>C6AFS2H8</td>
</tr>
<tr>
<td>CH</td>
<td>74.00</td>
<td>CH</td>
</tr>
<tr>
<td>C4AH22</td>
<td>722.72</td>
<td>C4AH13</td>
</tr>
<tr>
<td>C4AH10</td>
<td>658.62</td>
<td>C4AH10</td>
</tr>
<tr>
<td>M2AH10</td>
<td>645.50</td>
<td>M2AH10</td>
</tr>
</tbody>
</table>

where \( \text{b}_0^\text{OPC} \) is the initial OPC mass and it reads:

\[
b_0^\text{OPC} = m_{C3S} + m_{C2S} + m_{C3A} + m_{C4AF} + m_{CSS} + m_{C6A} + m_{C6AFS2} + m_{C6AFS2H8} + m_{CH} + m_{C4AH22} + m_{C4AH10} + m_{M2AH10}
\]

The total mass of binder (OPC and slag) \( b_0 \) and thus the mass fractions of the two components, \( x^\text{OPC} \) and \( x^\text{sl} \), respectively, can be considered as

\[
b_0 = b_0^\text{OPC} + b_0^\text{sl} \quad \text{(4)}
\]

\[
x^\text{OPC} = \frac{b_0^\text{OPC}}{b_0} \quad \text{and} \quad x^\text{sl} = \frac{b_0^\text{sl}}{b_0} \quad \text{(5)}
\]

The term \( m_{\text{sl}} \) refers to the unreacted oxides that are part of the composition of OPC besides the considered minerals, and \( x \) is the degree of hydration of OPC.

The degree of hydration of the OPC component will be the same as selected in [1], because all the samples are identical (in terms of composition, \( w_0/\beta_0 \) ratio, curing age and conditions, etc.).

2.2. The hydration of the slag component

A general equation describing the hydration of the slag component in OPC–slag blended cements is shown in Table 1 (Eq. (1.8)). The hydration products considered in this model are a Mg-containing phase (M2AH10 in saturated state), a Fe-containing phase (C6AFS2H18, in order to maintain the saturated state considered in the OPC model), the same two AFm phases (HO–AFm, C6AH10 and SO4–AFm, C6ASH14) considered for OPC hydration and C–S–H with a lower C/S ratio than the one formed by plain OPC and with a limited Al substitution. This model is based on the one presented by Chen and Brouwers [13,14], and modified in order to take into account newer findings from literature [15–18], which are detailed below. The fate of Mn in the slag hydration will not be considered in this study, for a number of reasons. Firstly, the model in [13,14] does not account for the contribution of manganese. Secondly, the oxidation state in which Mn is contained in the slag (Mn2+ as MnO or solid solutions (Fe,Mg,Mn)O [22] etc. or Mn3+ as MnO3 or a CaMn phase [23] or brownmillerite solid solutions [24]) is not known, so its hydration products cannot be predicted with any degree of accuracy.

An important observation to be made is that the formation of an AFt phase is not considered here. Recent studies [15–18] have shown that the amount of ettringite decreases with the increase of the amount of slag in the blended cement. Moreover, in [16,17] no ettringite was found in the samples after 90 days of curing in samples containing 75% and 90% slag [17] or 60% slag [16]. Therefore, in this model all sulphates present in the slag are considered to react with the alumina in the slag to form monosulphate. This reaction, together with the formation of the Fe-containing hydrogarnet, is considered to take priority over the other reaction involving the aluminates (molar relations are presented in Table 2).

It has also been observed that the C/S ratio of the formed C–S–H decreases as the proportion of slag in the mix increases [15,19,20]. Based on the data presented in [15], the following relation was fitted between the C/S ratio of the slag C–S–A–H, referred to as \( a \), and slag content (\( x^\text{sl} \)) in the mix:

\[
a = 1.7 - 0.5 \cdot x^\text{sl} \quad \text{(6)}
\]

The alumina from slag still available for hydration after the formation of monosulphate and hydrogarnet (Eq. (3.5) in Table 3) can afterwards enter the composition of C–S–H (Eq. (7) below and Eq. (3.2) from Table 3) and, if a sufficient quantity still remains, form HO–AFm (Eq. (3.6) in Table 3).

\[
\begin{align*}
\text{MOH}_{\text{sl}} &= n_{\text{MOH}_{\text{sl}}} \quad \text{(3.1)} \\
\text{MOSH}_{4\text{sl}} &= n_{\text{MOSH}_{4\text{sl}}} \quad \text{(3.2)} \\
\text{MOS}_{\text{sl}} &= n_{\text{MOS}_{\text{sl}}} \quad \text{(3.3)} \\
\text{MOSH}_{4\text{sl}} &= n_{\text{MOSH}_{4\text{sl}}} \quad \text{(3.4)} \\
\text{MOH}_{\text{sl}} &= n_{\text{MOH}_{\text{sl}}} \quad \text{(3.5)} \\
\end{align*}
\]

\[
\begin{align*}
\text{MOH}_{\text{sl}} &= n_{\text{MOH}_{\text{sl}}} + n_{\text{MOH}_{\text{sl}}} + n_{\text{MOSH}_{4\text{sl}}} - n_{\text{MOSH}_{4\text{sl}}} - n_{\text{MOS}_{\text{sl}}} - n_{\text{MOSH}_{4\text{sl}}} \\
\end{align*}
\]

where \( m_{\text{sl}} \) refers to the unreacted oxides that are part of the composition of OPC besides the considered minerals, and \( x \) is the degree of hydration of OPC.

The degree of hydration of the OPC component will be the same as selected in [1], because all the samples are identical (in terms of composition, \( w_0/\beta_0 \) ratio, curing age and conditions, etc.).
Table 3 lists the way all slag hydration products molar amounts \((\frac{n_{Ca}^{l} \cdot S_{A}^{l-n} \cdot H_{3}^{l-n}}{n_{Ca} \cdot S_{A} \cdot H_{3}})\), etc., Eqs. (3.1)-(3.5)) that can be computed from the initial slag composition.

### 2.3. The hydration of slag-blended cements

#### 2.3.1. The equilibrium of AFm phases

A first observation to be made is that, in the case of the hydration of the aluminate phases, there is no structural difference depending on whether the hydration product has been generated by the OPC or the slag component. However, as explained in [1], the HO–AFm phase is readily transformed to monosulfate \((SO_{4}^{2-} \text{AFm})\) in the presence of sulphates [27]. In the hydration model of OPC [1], the HO–AFm phase is formed only after depletion of sulphates. Therefore, when adding slag to the binder mix, the sulphate content of slag (assuming all sulphur in the slag to be in sulphate form) is considered to first transform the already existent HO–AFm (because of the faster hydration of OPC) to SO\(_{4}^{2-}\)-AFm. In this study, all Mg is considered to be bound into hydrotalcite, and therefore all Al needed for this reaction will be deducted from the Al available to form AFm phases (Table 3). The equilibrium between hydrotalcite and AFm formation is studied more in depth in [28,29].

#### 2.3.2. The equilibrium of the C–S–A–H phase

In the case of the C–S–A–H phase, its composition will reach an equilibrium between the composition of the slag-generated C–S–A–H and the OPC-generated one. Therefore, overall C/S and A/S ratios need to be computed. The value for the overall C/S ratio of C–S–A–H, formed by both the OPC and slag components of the blended cement can be computed as follows:

\[
\frac{n_{S}^{c} \cdot S_{l}^{l} \cdot H_{3}^{l} + n_{S}^{s} \cdot S_{l}^{l} \cdot H_{3}^{l}}{n_{C}^{c} \cdot S_{l}^{l} \cdot H_{3}^{l} + n_{C}^{s} \cdot S_{l}^{l} \cdot H_{3}^{l}} = \frac{1.7 \cdot n_{S}^{OPC} \cdot S_{l}^{l} \cdot H_{3}^{l} + a \cdot n_{S}^{s} \cdot S_{l}^{l} \cdot H_{3}^{l}}{n_{C}^{OPC} \cdot S_{l}^{l} \cdot H_{3}^{l} + a \cdot n_{C}^{s} \cdot S_{l}^{l} \cdot H_{3}^{l}}
\]

while the A/S ratio, an average \(b\), can be computed by substituting Eq. (10) into Eq. (8).

In case of insufficient alumina, the A/S ratio will be computed using the following equation:

\[
b = \frac{n_{S}^{s} \cdot S_{l}^{l} \cdot H_{3}^{l} + n_{S}^{l} \cdot S_{l}^{l} \cdot H_{3}^{l}}{n_{C}^{OPC} \cdot S_{l}^{l} \cdot H_{3}^{l} + a \cdot n_{C}^{s} \cdot S_{l}^{l} \cdot H_{3}^{l}}
\]

and the relations in Tables 2 and 3. Therefore, \(C_{S} \cdot S_{A} \cdot H_{3 + 1.5}\) would describe the composition of the global C–S–A–H phase.

#### 3. Chloride binding of the slag-blended cement pastes

##### 3.1. Binding isotherms

In the case of slag blended cements, the chloride binding ability will be due to the same hydration products as in the case of OPC. However, due to the differences in hydration, a number of changes will occur. The chloride binding of slag-blended hardened cement pastes will depend on three components: the chloride binding abilities of the OPC hydration products and of the slag hydration products, as well as the interaction between these two, which will result in a number of changes from the model presented in [1].

##### 3.2. Chloride binding – experimental data used in this study

The experimental results have been selected from [6]. The oxide compositions of the OPC and the slag used can be found in Table 7. In total 8 samples have been analysed – three hardened cement pastes (pure OPC) and five slag-blended cement hydrates pastes, with a slag content between 25% and 50%, and having various \(w_{0}/b_{0}\) ratios and curing ages. The composition of these samples and their computed sample masses and the attributed degree of hydration (both for the OPC component, \(x\), and the slag component, \(y\)) can be found in Tables 6 and 7. Also in Table 6 the parameters of the fitted chloride binding Freundlich isotherms, \(a_{x}\) and \(b_{x}\), are listed. Figs. 1 and 2 show the experimentally obtained chloride binding isotherms [6] for four slag-blended cement samples considered and two OPC pastes are included, split based on their \(w_{0}/b_{0}\) ratio. All the shown samples have the same curing age of 2 months before being exposed to the external chlorides. Fig. 1 shows three chloride binding isotherms of pastes with a \(w_{0}/b_{0}\) of 0.3 and slag contents of 0% (HCP1), 25% (S1) and 40% (S4). As expected, the chloride binding capacity increases with the increase of the slag content (Section 1). The same trend can be seen in Fig. 2, which presents three chloride binding isotherms of pastes with a \(w_{0}/b_{0}\) of 0.5 and slag contents of 0% (HCP2), 25% (S2) and 50% (S5). When comparing the two figures (for instance the S1 and S2 isotherms), it can be observed that the \(w_{0}/b_{0}\) ratio, and implicitly the degree of hydration, has a large influence on the chloride binding capacity.

---

**Table 6**

Characteristics of all hydrated cement pastes (selected from [6]): initial water to binder ratio, \(w_{0}/b_{0}\), curing age, slag ratio \((x^{d})\), the estimated degree of hydration of the OPC \((x)\) and the estimated degree of hydration of the slag \((y)\), the fitted Freundlich isotherm coefficients \((a_{x}\) and \(b_{x}\)), the final C/S ratio of the C–S–A–H phase \((a)\) and the mass of sample at 11% r.h. \((m_{spl})\), computed using Eqs. (2), (9), (12)).

<table>
<thead>
<tr>
<th>(w_{0}/b_{0})</th>
<th>Age (months)</th>
<th>(x^{d})</th>
<th>(x)</th>
<th>(y)</th>
<th>(a_{x})</th>
<th>(b_{x})</th>
<th>(a)</th>
<th>(m_{spl}) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP1</td>
<td>0.3</td>
<td>2</td>
<td>0</td>
<td>0.75</td>
<td>6.92</td>
<td>7.42</td>
<td>1.70</td>
<td>113.49</td>
</tr>
<tr>
<td>HCP2</td>
<td>0.5</td>
<td>2</td>
<td>0</td>
<td>0.80</td>
<td>7.72</td>
<td>7.49</td>
<td>1.70</td>
<td>114.39</td>
</tr>
<tr>
<td>HCP3</td>
<td>0.5</td>
<td>9</td>
<td>0</td>
<td>0.85</td>
<td>7.28</td>
<td>7.29</td>
<td>1.70</td>
<td>115.28</td>
</tr>
<tr>
<td>S1</td>
<td>0.3</td>
<td>2</td>
<td>0.25</td>
<td>0.75</td>
<td>0.60</td>
<td>7.25</td>
<td>1.58</td>
<td>109.13</td>
</tr>
<tr>
<td>S2</td>
<td>0.5</td>
<td>2</td>
<td>0.25</td>
<td>0.80</td>
<td>0.70</td>
<td>10.23</td>
<td>1.58</td>
<td>109.43</td>
</tr>
<tr>
<td>S3</td>
<td>0.5</td>
<td>9</td>
<td>0.25</td>
<td>0.85</td>
<td>0.75</td>
<td>9.36</td>
<td>1.58</td>
<td>109.36</td>
</tr>
<tr>
<td>S4</td>
<td>0.5</td>
<td>2</td>
<td>0.40</td>
<td>0.75</td>
<td>0.55</td>
<td>7.83</td>
<td>1.59</td>
<td>109.88</td>
</tr>
<tr>
<td>S5</td>
<td>0.5</td>
<td>2</td>
<td>0.50</td>
<td>0.80</td>
<td>0.50</td>
<td>9.94</td>
<td>1.45</td>
<td>110.70</td>
</tr>
</tbody>
</table>

In the case of these slag-blended hardened pastes (S1–S5), the mass of sample can be computed as follows:

\[
m_{spl} = m_{spl}^{OPC} \cdot x^{OPC} + m_{spl}^{sl} \cdot x^{sl}
\]
The chloride binding isotherms in this study will be termed either $C_{b, hp}$ for chloride binding abilities expressed in mg Cl\textsuperscript{−} /g hydration product conditioned to 11% r.h., or $C_{b, sl}$ for the chloride binding capacities expressed in mg Cl\textsuperscript{−} /g sample at 11% r.h., $m_{spl}$, as also employed in [1]. The term $n_{hp}$ refers to the molar amount of the specified hydration product, in moles, calculated using Tables 2–4. The mass of sample in grams at 11% r.h., $m_{spl}$, is computed as explained in Section 2.1. The following equation details the general relation between $C_{b, hp}$ and $C_{b, sl}$:

$$C_{b, hp} = C_{b, sl} \cdot \frac{n_{hp}}{m_{spl}} \cdot M_{11\% r.h.}$$ (13)

The three component chloride bindings (see Section 5) can be computed using the molar amounts in Tables 2–4 for $C_{b, hp}$, $C_{b, sl}$ and $C_{b, tot}$, respectively, the molecular masses from Table 5 and the mass of sample $m_{spl}$ from Table 6.

The chloride concentration of the external solution, $c$, is always expressed in mol Cl\textsuperscript{−} /l solution and considered to be in equilibrium with the pore solution. Therefore, the terms of “external”, “free” or “equilibrium” chloride concentration will be used interchangeably throughout this study.

4.1. Chloride binding capacity of the aluminate phases in slag-blended cements

Firstly, the chloride binding of the aluminate phases will be considered to be described by the same equations detailed in [1]. The “simplified version” of this model will be used, which does not take into consideration the contribution of CH and FS (Friedel’s salt, 3CaO.Al\textsubscript{2}O\textsubscript{3}.CaCl\textsubscript{2}.10H\textsubscript{2}O) to the physical binding of chlorides. The reason for this choice is the low contribution of these two phases in [1] (around 3% of the total bound chlorides), as well as ease of use. Moreover, the surface binding of chlorides by these two hydrates is controversial, and no data about their binding capacities in systems where hydrates with more negative surfaces (C–S–A–H with various C/S ratios, see following section) coexist. Another difference from the model presented in [1] is that the total amounts of HO–AFm and SO\textsubscript{4}–AFm (just as C–S–A–H) generated by both the hydration of OPC and the one of the slag (Table 4), will be considered able to bind chlorides. The isotherms describing the chloride binding capacity of HO–AFm and SO\textsubscript{4}–AFm from OPC are given in Table 8 (Eqs. (8.2) and (8.1), respectively) and are based on the findings in [30,31], where the Cl-containing phase formed is considered to be Friedel’s salt. Another possible phase is Kuzel’s salt (3CaO.Al\textsubscript{2}O\textsubscript{3}.2CaCl\textsubscript{2}.1H\textsubscript{2}O) [32], but to the authors’ knowledge a chloride binding isotherm for its formation has not been measured in literature.

Another phase which is considered to be able to bind chlorides is hydrotalcite (HT) [28]. However, to the authors’ knowledge, a chloride binding isotherm of HT has not been quantified in literature. Kayali et al. [28] present the chloride binding of HT at only one chloride concentration (3%) and only after 24 h (compared to the 14 days usually used for obtaining chloride binding isotherms [6]). Another aspect of quantifying the chloride binding capacity of hydrotalcite would be the variation in the Al\textsuperscript{3+}/(Al\textsuperscript{3+} + Mg\textsuperscript{2+}) ratio of HT, which is known to vary between 0.2 and 0.33 [28].

Moreover, the particular slag considered in this study has a very low MgO content (0.66% by mass of slag, see Table 7) compared to the ones cited in literature (up to 12% by mass in [20], 6.3% by mass in [28], between 7% and 13% by mass in [29]). Therefore, the influence of the chloride binding of HT is minimal in this case and it will not be considered further.
4.2. Chloride binding capacity of the C–S–A–H phase in slag-blended cements

As explained in Section 2.2, the C–S–A–H phase generated by slag-blended cements will have two main differences from the one formed by the hydration of pure OPC: the C/S ratio and the A/S ratio. However, as explained in Section 2.1, the value of 1.7 for the C/S ratio, considered for the C–S–H formed considering the hydration of OPC in [1], actually corresponds to the C/(S + A) ratio. Therefore, the C/(S + A) ratio will be taken into account also for the chloride binding capacity of the C–S–A–H generated by the slag component.

A modification from the $C_b^{\text{C–S–A–H}}$ isotherm presented in [1], will be the use of a simplified relation which does not take into account the $C_b^{\text{C–S–A–H}}$ ratio in OPC for the slag-generated C–S–A–H chloride binding capacity. The C–S–H isotherm proposed in [1] was a combination of two isotherms proposed by Zibara [6] for C–S–H formed by C2S and C3S, respectively. However (as explained in [1]), there is no structural difference between the final products of hydration. In [1], a combination of the two isotherms was used for the sake of precision. The same isotherm (Eqs. (8.3)–(8.5)) will be used for the chloride binding of C–S–A–H when referring to the individual hydration of OPC. However, the two isotherms proposed by Zibara [6] are almost identical. Therefore, the following relation was selected to further represent the chloride binding of a C–S–A–H generated by slag:

$$
C_b^{\text{C–S–A–H}} = \lambda \cdot 6.65 \times 10^{334} 
$$

As the selected chloride binding isotherm for C–S–A–H is valid for a C/(S + A) ratio of 1.7, a correction needs to be done for lower values. Viallis-Terrisse [32] has studied the chloride binding ability of lymphilized C–S–H gels with C/S ratios between 0.65 and 1.50, using a NaCl solution with the concentration of 0.5 M. The results have shown that when the C/S ratio decreases from 1.55 to 1.2, the amount of bound chlorides increases. When the C/S ratio further decreases up to 0.8, the chloride binding capacity also slightly decreases, the trend accentuating (higher slope of the linear fit) for C/S ratios between 0.8 and 0.6. Due to the use of lymphilized C–S–H gels, the measured amounts of bound chlorides were very different than when using alcohol for drying the gels. Therefore, just to the ratio between the bound chlorides amounts is used here, since this is considered to be correct, as a ratio of results that follow the same experimental protocol. Fig. 3 shows these ratios as a function of the C/S ratio in C–S–H and the fitted parabolic equation, extrapolated to a C/S ratio of 1.7, which is considered to have a ratio of unity (this point is also part of the fit and figures as a hollow circle in Fig. 3). The result of this equation will be considered as the coefficient $\lambda$ by which the chloride binding of the C–S–A–H phase needs to be multiplied in order to account for the differences in their C/S ratios. This coefficient will be calculated in the same way for both the OPC–slag blended cement samples, as well as the “slag only” samples.

$$
\lambda = -2.1381 \left( \frac{a}{1 + b} \right)^2 + 4.6139 \cdot \frac{a}{1 + b} - 0.6646 
$$

5. Chloride binding isotherms

Three types of chloride binding isotherms will be computed in this study – for the individual hydration of OPC (described in Table 2) $C_b^{\text{OPC}}$, the hydration of the slag component while only the role of CH produced by the OPC hydration is taken into account (molar amounts from Table 3) $C_b^{\text{sl}}$ and the total chloride binding of both components $C_b^{\text{total}}$ using the amounts in Table 4, respectively. In all three cases, the general formula for the chloride binding capacity of the hydrated paste is expressed by:

$$
C_b = C_b^{\text{OPC}} + C_b^{\text{sl}} + C_b^{\text{HO–AFm}}
$$

where the three component chloride bindings can be computed using the molar amounts in Tables 2–4 for $C_b^{\text{OPC}}, C_b^{\text{sl}}$ and $C_b^{\text{total}}$, respectively.

5.1. Chloride binding of the slag-blended cement samples

In this section, the $C_b^{\text{total}}$ isotherms will be computed for the S1–S5 samples (composition in Table 6) by computing the individual chloride binding isotherms of C–S–A–H, SO4–AFm and HO–AFm as described in Section 4 and using the molar amounts computed in Table 4. In other words, the total amounts of hydration products generated by the hydration of the slag-blended cements will be considered, including their interactions as described in Section 2.3.

Fig. 4 shows how the computed $C_b^{\text{total}}$ for S4 (composition from Table 6) compares to the experimental data, as well as the contribution of the SO4–AFm and C–S–A–H phases. In this case, the C–S–A–H phase contributes about two thirds of the total chloride binding capacity of the paste. Furthermore, these two total contributions are split into their components in order to see the influence of the slag hydration products on the total chloride binding ability of the paste. Figs. 5 and 6 show this breakdown for both the SO4–AFm and C–S–A–H phases, respectively. From Fig. 5 it can be seen that the contribution of the SO4–AFm phase determined by the hydration of slag is slightly higher than the one of OPC. This can be explained by the fact that, as explained in Section 4.1 and Table 4, there are two mechanisms considered for the formation of SO4–AFm through the hydration of slag, one involving the aluminate phase generated by the dissolving of the
slag itself, and the second one coming from the conversion of HO–AFm generated by the hydration of OPC into SO4–AFm.

In the case of the C–S–A–H phase (Fig. 6), the trend is reversed: the contribution of the OPC-generated C–S–A–H is slightly higher than the one generated by the slag. However, both these isotherms take into consideration the $k$ coefficient (see Eq. (15)), which explains the increase of the C–S–A–H chloride binding capacity. There is no structural difference between the two C–S–A–H phases, only the computed amounts are dependent of the C and the S contents of the slag.

Fig. 7 shows the breakdown of chloride binding capacity between the four mentioned phases as a function of the free chloride concentration. As it can be seen, the contribution of the C–S–A–H phase slightly decreases from a total of 70% of the bound chlorides (39% the OPC-generated C–S–A–H and 31% the slag-generated one) at 0.5 M external chloride concentration to 63% at a free chloride concentration of 1.8 M (35% the OPC-generated C–S–A–H contribution and 28% the slag-generated amount). On the contrary, the contribution of the SO4–AFm phase shows an increase from 30% of the bound chlorides (13.2% from the OPC-generated SO4–AFm and 16.8% from the slag hydration) at 0.5 M external chloride concentration to 37% at a free chloride concentration of 1.8 M (16.2% and 20.7% from the OPC-generated SO4–AFm and the slag-generated one, respectively).

5.2. Evaluation of the contribution of the slag component to chloride binding

As explained in Section 2.3 and quantified in Table 4, $C_{b}^{\text{total}}$ will not simply be a sum of $C_{b}^{\text{OPC}}$ and $C_{b}^{\text{sl}}$, due to the fact that the hydration of the OPC-component and that of the slag component do not progress independently, as explained in Section 4. Therefore, it can be considered that the chloride binding capacity of slag-blended hydrated pastes consists of three components: one due to the hydration products of OPC remaining unmodified by the slag hydration (so just SO4–AFm and C–S–A–H when the $k$ coefficient is set to unity), one due to the hydration products of the slag while only the role of CH produced by the OPC hydration is taken into account (actually $C_{b}^{\text{sl}}$), and one which represents the interaction of the two components of the binder.

In order to quantify this third component, three other equations will be used. The interaction between the OPC and the slag component of the binder can be described in terms relevant to their chloride binding abilities by two phenomena: the decrease of the C/(S + A) ratio of C–S–A–H (so through the $i$ coefficient in Eq. (8.5)) and the consumption of the HO–AFm phase by the sulphate ions generated by slag. Therefore, the $C_{b}^{\text{sl}}$ will be compared to the following three isotherms:

$$C_{b}^{\text{diff}} = C_{b}^{\text{exp,total}} - C_{b}^{\text{exp,OPC}} \cdot x_{\text{OPC}}$$ (17)

$$C_{b}^{\text{corr1}} = C_{b}^{\text{diff}} - C_{b}^{\text{OPC}} \cdot (\lambda - 1)$$ (18)

$$C_{b}^{\text{corr2}} = C_{b}^{\text{corr1}} + \frac{n_{\text{m,AFm}}}{M_{\text{11Y},\text{CH},\text{AFm}}} \cdot \frac{C_{b}^{\text{sl}}}{C_{b}^{\text{SO4–AFm}}} - C_{b}^{\text{sl}}$$ (19)
The isotherm $C_{\text{corr1}}$ represents the difference between the total chloride binding ability of the slag-blended hydrated paste and the chloride binding of its OPC component, while taking into account the OPC ratio in the blended cement. If the interactions in Section 2.3 would not be taken into account (so the hydration would be described solely on the basis of Sections 2.1 and 2.2 as two separate processes – the hydration of the OPC-component and that of the slag-component, respectively), the $C_{\text{corr1}}$ should be equal to $C_{b}^6$.

Since it has been explained that this approach would be over-simplified, $C_{\text{corr1}}$ is computed to account for the influence of the decreased $C$/S ratio of the $\text{C–S–A–H}$ of the OPC component (Section 2.3.2). This isotherm considers the fact that the $\text{C–S–A–H}$ generated from the OPC hydration has a higher $C$/S ratio and therefore a decreased chloride binding (see Section 4.2) compared to the $\text{C–S–A–H}$ of the slag-blended cement hydration. A correction is therefore applied to $C_{b}^6$ by subtracting this increase which is due to the $\lambda$ coefficient (see Eq. (8.5)).

The third isotherm, $C_{\text{corr2}}$, further accounts for the transformation of HO–AFm to $\text{SO}_4$–AFm, as described in Section 2.3.1. In order to achieve this, the contribution of OPC-generated HO–AFm to the chloride binding is subtracted, and instead the influence of the newly-formed $\text{SO}_4$–AFm is added. The influence of this transformation on the mass of the sample is considered to be negligible. In this way, both interactions considered in Section 2.3 are accounted for, and the contribution of the slag component of the blended cement can be validated by comparing the $C_{\text{corr2}}$ and $C_{b}^6$ isotherms.

Fig. 8 illustrates the $C_{\text{corr1}}^\text{diff}$, $C_{b}^6$ and $C_{\text{corr2}}^\text{diff}$ isotherms for the sample S4, together with the $C_{b}^6$ isotherm for comparison. Initially, the difference between the $C_{\text{corr1}}^\text{diff}$ and $C_{b}^6$ is quite significant. When $C_{\text{corr1}}^\text{diff}$ is computed to account for the $\lambda$ coefficient contribution, the difference to $C_{b}^6$ becomes lower. With the introduction of $C_{\text{corr2}}^\text{diff}$, the match to $C_{b}^6$ becomes very good. Therefore, it can be concluded that, indeed, the interaction between the hydration of the OPC and that of the slag in terms of chloride binding ability can be estimated accurately by the decrease of the $C/(S + A)$ ratio of $\text{C–S–A–H}$ and the consumption of the HO–AFm phase by the sulphate ions generated by the slag dissolution. Moreover, this match proves that the model works independently for describing the chloride binding ability of the slag component, and also that the model used to quantify the hydration of the slag is valid.

Fig. 7. Breakdown of bound chlorides by hydration products as a function of equilibrium chloride concentration in the pore solution applied to sample S4 (see Table 6). Isotherms are described in Sections 4 and 5.

Fig. 8. Chloride binding capacity of each hydrated paste (see Table 6) with experimental values at free chloride concentrations of 0.5 M and 1.8 M (see Section 5.2).

6. Comparison with experimental data and other models from literature

The only non-kinetic chloride binding model which could be found in literature is the one of Dhir et al. [7]. While this model takes into account the slag percentage in the slag-blended cement and the concentration of free chlorides, it does not take into account other parameters such as w/b, curing age etc. Therefore, for the samples S1, S2 and S3, for instance, the prediction will be the same. The equation describing this model is:

$$C_{\text{Dhir}}^\text{b} = \left[ -22.21 \cdot (x^1)^2 + 39.45 \cdot x^1 + 3.36 \right] \cdot c + \left[ 6.84 \cdot (x^1)^2 - 6.40 \cdot x^1 + 3.64 \right] $$

and will be used for comparison purposes together with the $C_{\text{b}}^{\text{total}}$ values and the experimental values (Freundlich isotherm parameters in Table 6) at two different free chloride concentrations. Here, the concentration of 0.5 M was chosen as significant, being the usual chloride concentration of sea water [1]. The second chosen concentration is 1.8 M, as used in the Rapid Chloride Migration test [4]. Fig. 9 shows the experimental isotherms, the $C_{\text{b}}^{\text{total}}$ and $C_{\text{b}}^{\text{sl}}$ at
these two free chlorides concentrations. The results show that the proposed model estimates the binding chloride ability of slag-blended pastes with enough accuracy, the relative errors to experimental values being between 3.5% and 29%, with an average of ~17% over the whole interval of free chloride concentrations. These errors can have a number of possible sources, including the errors of the initial OPC chloride binding model of ~8% [1], the scatter of the experimental data used, the estimation of hydration degree based on age of the sample and its composition and the role of slag-generated alumina during the hydration process. The latter parameter was observed to have the highest impact on the estimation of chloride binding ability. The results presented in this study are based on the hydration of a slag with a low A/S ratio (as categorized by [15,19,20], A/S = 0.16 in the slag). For slags with a higher initial A/S ratio, the incorporation of A in the C–S–A–H structure will also be increased. Moreover, if the alumina is sufficient, HO–AFm could be formed after the complete reaction of the sulphates, and also contribute to the chloride binding. As explained in [1], the high chloride binding ability of HO–AFm will have a significant influence on the total bound chlorides, even if this hydration product is formed only in small quantities. However, the complex relationship between the AFm phases in the hydrated cement matrix (as detailed in [1]) can mostly account for the underestimation of the chloride binding capacity.

Also from Fig. 9 it can be seen that the model proposed by Dhir et al. [7] overestimates the chloride binding capacity of the slag-blended cement pastes, with relative errors between 40 and 100% for a free chloride concentration of 0.5 M. For larger free chloride concentrations, however, the model predicts 3–3.5 times more bound chlorides than what is measured experimentally.

7. Summary and conclusions

Two hydration models [10–14] were combined in this study in order to describe the phase assemblage of a hydrated slag-blended cement paste. New insights into the hydration products of slag-blended cements [15–20,27] were employed to explain the interaction between the two components of the binder: the OPC and the slag, respectively. Separate hydration degrees were estimated for the two components [26] and the mass of each sample at 11% r.h. was computed accordingly. The considered phases able to bind chlorides are the AFm phases and the C–S–A–H phase. The latter one is considered to be able to incorporate alumina in its structure [13–15,19,20], and its C/S and A/S ratios are taken into account when estimating its chloride binding capacity [32].

The chloride binding capacity of slag-blended cement pastes is considered to be due to three processes: the hydration of the OPC component, the one of the slag component, which both generate chloride-binding hydrated phases, and the interaction of the two, which modifies the final phase assemblage. This third component can, in its turn, be attributed to a number of factors: the decrease of the C/S ratio of the C–S–A–H phase, the incorporation of alumina in the C–S–A–H structure, the transformation of HO–AFm into SO4–AFm in the presence of sulphates and the decreasing amount of ettringite formed with the increase of the slag content of the blend. All these factors are quantified in the present model, in order to ensure the accuracy of the chloride binding estimation. The importance of quantifying separately the chemically and physically bound chlorides in order to evaluate the influence of the slag composition is also underlined in [33]. The reduction of the C/S ratio of the C–S–A–H phase as well as the influence of the alumina content of the slag are also concluded in [34,35].

When taking into consideration the breakdown of the bound chlorides by hydrated phase, it is observed that the C–S–A–H phase is roughly responsible for two thirds of the bound chlorides, the rest being attributed to the AFm phases. These percentages vary slightly, the contribution of C–S–A–H decreasing by ~10% with the increase of the free chlorides concentration between 0.5 and 1.8 M, while the contribution of SO4–AFm increases by ~20%. The contribution of the AFm phases could be much higher, if the considered slag had a higher initial A/S ratio. According to [25], the slag considered in this study has an intermediate A/S ratio. Its increase would determine multiple changes on the microstructure of the hydrated paste, the A/S ratio of C–S–A–H and the amount of AFm phase being the most important.

Besides the A content, the C content of the slag is also important for the final C/S ratio of the C–S–A–H phase, while its amount is influenced by the S content of the slag. Perhaps the most influential factor (together with the A content) on the chloride binding ability of the past is the S content of the slag. The sulphate content will determine the amount of HO–AFm formed, which is the hydration product with the highest chloride binding capacity from all hydration products studied in this paper and in [1]. Therefore, just like in the case of the OPC composition, but perhaps even more important, the composition of the slag is crucial to the maximum chloride binding capacity of the hydrated paste.

The presented model takes into account all these factors, together with the w/o/b ratio and age of sample, through the two degrees of hydration estimated. By taking into consideration these compositional and curing factors, the accuracy of the model is highly improved from a previous model from literature, which only takes into account the slag content of the mix. This holds true for all free chloride concentrations considered, but the difference becomes more important at higher free chloride concentrations.

The importance of the content of both aluminate phases and sulphates in the initial binder composition is highlighted by the findings of this study.

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References


