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Chloride binding related to hydration products
Part I: Ordinary Portland Cement

M.V.A. Florea [*], H.J.H. Brouwers

Department of the Built Environment, Unit Building Physics and Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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ABSTRACT

This study attempts to correlate the total amount of chloride bound in concrete with the amounts bound by different hydration products. New insights in the quantities of the hydration products formed will be used in order to predict the phase assemblage of hardened cement pastes. The two main chloride binding mechanisms are considered — through physical adsorption and through chemical reactions. Chloride binding isotherms are used, taking into account the external chloride concentration and the quantity of each hydration product formed. A distinction is made between the chloride binding capacities of monosulfate and hydroxy-AFm. Two new models for the maximum chloride binding ability of a hardened cement paste are proposed — a basic one, using only AFm and C-S-H isotherms, and an extended one which also considers the ability of portlandite and Friedel's salt to physically adsorb chlorides. Results obtained using these models are within 10% of collected experimental data.

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 chloride ions [1–3].

There are several factors that influence chloride binding. Perhaps the most important one is the way chloride ions are added to the concrete mix. Using this criteria, chloride ions can be divided in two categories: internal chlorides (when the chloride solution is intermixed with the cement powder [4–6]), or external chlorides (when chloride ions intrude in already hardened cement paste or concrete [6–9]). Since the amount of internal chlorides is restricted and their use is currently discouraged, this study will focus on external chlorides, as the more frequent situation in practice.

There is an important distinction to be made between the different sources of chloride ions. The most studied two salts are calcium chloride and sodium chloride, which give different results due to their differences in the binding mechanisms of the Cl^- ion [6,10,11]. 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 chloride attack on reinforced concrete structures. The typical concentration of NaCl in seawater is fairly constant (e.g. the Atlantic Ocean: 3.6% mass, the North Sea: 3.3%, the Persian Gulf: 4.3%) [12]. These concentrations (between 3.3 and 4.3%) correspond to a range of 0.6–0.7 mol Cl^-/l seawater. Another reason for investigating NaCl as a source of chloride ions is its use in the rapid chloride migration (RCM) test [46]. 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 (2 M) immersion solution [9]. Furthermore, in the case of salty lakes, the chloride concentration can be over 3 M [13]. In order to incorporate all values mentioned above, the range of NaCl concentration used in this study is 0–3 M.

Researchers have studied chloride binding using various approaches. Some studies dealt with existing concrete structures [14,15], while others preferred the use of mortars, due to their less complicated structure [9,16]. The method that produces the best results is to use cement paste, in which the presence of aggregates cannot interfere with the measurements [9,17,18]. Another approach was to study pure hydration products [7,8,19,20]. Through this method important information about the mechanisms through which single hydration products bind chlorides were gathered. This study will use data collected in literature through most of these methods to predict the chloride binding of cement pastes.

Ordinary Portland Cement (OPC) is chosen as binder throughout the study, since it is the most abundantly used cement type and the most basic system in terms of hydration modeling that still contains all phases involved in chloride binding. Other cementitious materials studied in literature include grounded blast furnace slag, fly-ash or silica fume [2,6,13,21,22]. All these materials have different hydration

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[*] Corresponding author. Tel.: +31 40 247 46 87; fax: +31 40 243 85 95.
E-mail address: m.v.a.florea@tue.nl (M.V.A. Florea).

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mechanisms and will not be considered in the present paper, but will be addressed in future work.

The two main chloride binding mechanisms – through physical adsorption and through chemical substitution – were considered, along with estimating the amount of chlorides in the pore solution. Out of the considered hydration products in OPC hardened pastes, two hydrated phases are best known to be able to bind chloride ions — the calcium silicate hydrate (C-S-H) phase [7–9] and the AFm phase [5,7,8,23,24]. Beside these, the chloride binding capacities of portlandite and ettringite are debated in literature [8,16,25,27]. Friedel's salt, a compound formed through the interaction of other AFm phases and intruding chlorides, is considered to be also able to physically adsorb chlorides on its surface [26].

2. The paste model

The three main phases of a hardened cement paste (unreacted cement, unreacted water and its hydration products) and its porosity can be studied in terms of mass and volume for a given hydration degree. When clinker phases hydrate individually, so not in combination with others, their degree of hydration can vary significantly. This is important when considering the hydration degree of individual phases rather than OPC. On the other side, for longer curing times, clinker minerals can be considered to react more or less congruently when hydrating together in cement pastes [28]. For the hydration of OPC pastes, a global degree of hydration can be assumed for all clinker minerals, when hydration has progressed over 50% [29,30,47]. Typical hydration kinetics at ambient temperature for pure clinker minerals (C_3S, C_2S, C_3A with and without added gypsum, C_4AF), as well as for an OPC, are given in [28]. Another important point to consider is that the hydration degree will increase with the increase of the water to binder (w_0/b_0) ratio used for the hydration of an OPC paste [31].

In order to predict the hydration products formed, a recent model proposed by Brouwers [29,30,47] will be used. The reactions that describe the saturated hydration of OPC are presented in Table 1. These reactions assume that no carbonation of the paste has taken place. While the model of Brouwers [29,30,47] allows for different carbonation degrees, this option has not been taken into consideration in the current study, due to the insufficient data on the effect of carbonation of chloride binding. Most experimental data has not taken into account the possibility of carbonation or did not measure the extent of it [9,25]. The relations in Table 2, which are deduced from the chemical equations in Table 1, can be used to calculate the molar amounts of hydration products. These are the maximum amounts that can be formed after a complete hydration of cement. Since this is usually not the case, each amount has to be multiplied by the degree of hydration, α.

The mass of reacted cement, b, can be calculated using the following relation:

$$b = \alpha(b_0 - m_{UO}) \tag{1}$$

where b_0 is the initial mass of cement before the start of hydration. The initial mass of cement is made out of the masses of clinker minerals (m_{C_3S}, m_{C_2S} etc.) and that of the unreacted oxides, m_{UO}:

$$b_0 = m_{C_3S} + m_{C_2S} + m_{C_3A} + m_{C_4AF} + m_{C\bar{S}} + m_{UO}. \tag{2}$$

Table 1
The chemical equations describing the saturated hydration of OPC, as described in [29,30,47].

$C_3S + 4.5H \rightarrow C_{1.7}SH_{3.2} + 1.3CH$
$C_2S + 3.5H \rightarrow C_{1.7}SH_{3.2} + 0.3CH$
$C_3A + C\bar{S} + 14H \rightarrow C_4A\bar{S}H_{14}$
$C_3A + CH + 21H \rightarrow C_4AH_{22}$
$C_3A + 3C\bar{S} + 36H \rightarrow C_6A\bar{S}_3H_{36}$
$C_4AF + 2C_3S + 22H \rightarrow C_6AFS_2H_{18} + 4CH$
$C_4AF + 2C_2S + 20H \rightarrow C_6AFS_2H_{18} + 2CH$

Table 2
Molar relations between the amounts of hydration products and the mineral composition of OPC, as described in [29,30,47].

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

These equations are used when the hydration of individual phases is considered, in Section 5.

The mass of the hydration products can also be expressed as a function of the mass fractions of clinker minerals in the binder. These mass fractions by weight of binder of the clinker minerals have the following expressions:

$$x_{C_3S} = m_{C_3S}/b_0; \quad x_{C_2S} = m_{C_2S}/b_0; \quad \text{etc.} \tag{3}$$

where Eq. (1) has been inserted.

Knowing how many moles of each hydration product were formed (see Table 2), their masses can also be computed using their molecular masses:

$$m_{C_4A\bar{S}H_{14}} = n_{C_4A\bar{S}H_{14}} M_{C_4A\bar{S}H_{14}}; \quad m_{CH} = n_{CH} M_{CH} \ \text{etc.} \tag{4}$$

The molecular masses of hydration products formed under saturated conditions are listed in Table 3. Using these molecular masses, the molecular masses of the clinker minerals from Table 4 and Eq. (4), the mass relations can be computed from the molar relations as shown in Table 2. For ease of use, Table 5 lists the modified formulas for computing the mass of hydration products formed, relative to the mass of reacted binder, for saturated conditions, meaning 100% relative humidity (rh).

A number of experimental studies found in literature [8,9] determine the chloride binding capacity of hardened cement paste on samples dried at 11% rh. When a saturated hardened cement paste sample is dried to 11% rh, some of the hydration products modify their water content [33]. The corresponding formulas and molecular masses can also be found in the second column of Table 3. Upon 11% rh drying, the mass of the hydration products changes due to the water loss, but the molar quantities remain the same. Therefore, the mass of the hydration products after 11% rh drying can be calculated using the equations listed in Table 2 and the molecular masses from Table 3, Eq. (4) thus becoming:

$$m_{CSH} = m_{C_{1.7}SH_{2.1}} = n_{C_{1.7}SH_{3.2}} M_{C_{1.7}SH_{2.1}}; \quad m_{C_6A\bar{S}_3H_{12}} = n_{C_6A\bar{S}_3H_{36}} M_{C_6A\bar{S}_3H_{12}} \ \text{etc.} \tag{5}$$

Knowing the hydration degree and the mass of the formed hydration products, the mass of the whole sample dried to 11% rh can be calculated. The sample dried to 11% rh consists of dried hydration

Table 3
The formula and molecular mass for each hydration product formed in saturated state [29,30,47] and after drying at 11% rh [33].

Saturated state		Dried state	
(100% rh)		(11% rh)	
Formula	[g/mol]	Formula	[g/mol]
$C_6A\bar{S}_3H_{36}$	1327.34	$C_6A\bar{S}_3H_{12}$	894.98
C_4AH_{22}	722.72	C_4AH_{13}	560.58
$C_{1.7}SH_{3.2}$	213.09	$C_{1.7}SH_{2.1}$	193.27
CH	74.00	CH	74.00
$C_6AFS_2H_{18}$	1042.67	$C_6AFS_2H_8$	862.47
$C_4A\bar{S}H_{14}$	658.62	$C_4A\bar{S}H_{10}$	586.56

Table 4
The formula and molecular mass for each clinker mineral considered [33].

Formula	[g/mol]
C_3S	228.33
C_2S	172.25
C_3A	270.20
C_4AF	485.97
$C\bar{S}$	136.14

products (see Table 3), unreacted cement minerals and uncombined oxides. The formula for the mass of the whole sample after drying to 11% rh is given as:

$$\mathrm{m_{spl}} = \mathrm{m_{C_{1.7}SH_{2.1}}} + \mathrm{m_{C_4A\bar{S}H_{10}}} + \mathrm{m_{C_6AFS_2H_8}} + \mathrm{m_{C_6A\bar{S}_3H_{12}}} + \mathrm{m_{C_4AH_{13}}} + \mathrm{m_{CH}} + (1-\alpha)(\mathrm{b_0}-\mathrm{m_{UO}}) + \mathrm{m_{UO}} \tag{6}$$

where m_{UO} can be determined from Eq. (2).

3. Chloride ions in cement paste

3.1. Binding isotherms

Chloride ions ingressed in the hardened cement paste can be divided into two main groups: free chloride ions, present in the pore solution, and bound chloride ions, attached to various hydration products. The relationship between the concentration of free chloride ions in the pore solution, c, and expressed in mol Cl^-/l of pore solution, and bound chlorides can be described using chloride binding isotherms. Tang and Nilsson [9] have concluded that Freundlich isotherms can be used at concentrations of external chlorides greater than 0.01 M, while Langmuir isotherms are better suited for lower concentrations, below 0.05 M. Zibara [8] also employed both Freundlich and Langmuir isotherms in describing the experimental results, and preferred the Freundlich isotherm expression throughout the study. Hirao et al. [25] have chosen both Freundlich and Langmuir isotherms to describe the chloride binding capacity of hydrated phases. Since both types of isotherms are used in different studies, also here both correlations will be addressed.

3.2. Chloride binding — experimental data used in this study

All chloride binding isotherms presented in this study were obtained under laboratory conditions using the equilibrium method [8,9,25]. All experiments were conducted at ambient temperature (around 22 °C).

Several OPC compositions have been selected from [8] and [9] in order to test the accuracy of the chloride binding predictions. These compositions have been selected following a number of guidelines mentioned for OPC in literature. According to the standard EN 197–1:2000 [34], there are a few compulsory requirements (Table 6). Lea's Chemistry [28] mentions usual composition ranges for OPC, while [12] gives the typical values of composition of OPC, in terms of clicker minerals percentages (Table 7). OPC compositions not complying with the values mentioned in Tables 6 and 7 were not considered in this study, as being atypical of commercially available compositions. Another important reason for the exclusion of certain cement compositions was the expected change in the phase assemblage of the hydration products, when the considered cement does not comply with usual compositional ranges.

Table 5
Relations between the mass of hydration products and the mass fractions of OPC minerals, as described in [29,30,47].

$$m_{C_6\mathrm{AFS_2}H_{18}}/b = 2.146x_{\mathrm{C_4AF}}$$
$$\mathrm{m_{C_6A\bar{S}\ _3H_{36}}/b = 2.437x_{C\bar{S}}}$$
$$\mathrm{m_{C_4A\bar{S}H_{14}}/b = 1.209\,x_{C\bar{S}}}$$
$$m_{C_4AH_{22}}/b = 2.675x_{C_3A}-2.654x_{C\bar{S}}$$
$$m_{C_{1.7}SH_{3.2}}/b = 0.933x_{C_3S} + 1.237x_{C_2S}-0.877x_{C_4AF}$$
$$m_{\mathrm{CH}}/b = 0.422x_{C_3S} + 0.129x_{C_2S}-0.274x_{C_3A} + 0.213x_{C_4AF} + 0.271x_{C\bar{S}}$$
$$m_{\mathrm{UO}}/b = 1-x_{C_3S}-x_{C_2S}-x_{C_3A}-x_{C_4AF}-x_{C\bar{S}}$$

Table 6
Requirements for OPC composition mentioned in the EN 1–197:2000 standard [34].

$$m\%_{C_2S} + m\%_{C_3S} \geq 2/3$$
$$\frac{m\%_{CaO}}{m\%_{SiO_2}} \geq 2$$
$$m\%_{MgO} \leq 5\%$$

OPC compositions termed OPC 1, OPC 2 and OPC 3 are selected from [8], where their original identifiers were “C2”, “C3” and “Control” respectively. OPC 4 is the one considered by [9] in their experiments. Using Bogue's equations, the mineralogical composition has been calculated for all considered OPCs, the resulting compositions being given in Table 8.

Zibara [8] has fitted Freundlich isotherms for hardened pastes obtained from the OPC 1 ÷ OPC 3 compositions (see Table 8) with different $\mathrm{w_0/b_0}$ ratios: 0.3, 0.5 and 0.7. In [9], the authors present three Freundlich-type binding isotherms for the OPC 4 paste, for three different $\mathrm{w_0/b_0}$ ratios, of 0.4, 0.6 and 0.8. The composition of all these hardened cement pastes are given in Table 9, together with their estimated hydration degree at the end of the sorption experiment and their initial mass of sample dried at 11% rh, $\mathrm{m_{spl}}$, calculated using Eq. (6). The hydration degree is estimated based on the $\mathrm{w_0/b_0}$ ratio and the age of sample at the time of immersion in the chloride solution for the HCP1÷HCP5 compositions. The hydration degree values for HCP6÷HCP8 are taken from [9]. Also mentioned in Table 9 are the fitted α_F and β_F values for these isotherms. Figs. 1 and 2 show the experimental binding isotherms of all eight compositions.

4. The chloride binding ability of OPC hydration products

The AFm compounds are generally known to be able to bind chloride ions through chemical substitution [1,2,5,7,8,23]. The C-S-H phase is considered to physically bind chlorides due to its high specific surface values [7,35–37]. The role of ettringite in chloride binding is highly debated [16,23,25], the same being true for portlandite [25,26]. Friedel's salt (FS) is a hydrated phase formed under the attack of chloride ions, but which is, in its turn, considered in [26] to be able to physically bind chlorides.

4.1. The chloride binding ability of the AFm phase

Justnes [2,12] concluded, based on an extensive literature review, that the chloride binding capacity of cementitious materials is dominated by the content of calcium aluminates and calcium aluminoferrites (through the formation of Friedel's salt, $3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$). However, Neville [12,28] 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. For this situation, that study states that the formation of Friedel's salt or chloroferrite from the aluminates takes place rapidly during

Table 7
Compositional range for Ordinary Portland Cements [12,28].

Oxide	Hewlett [28]	Neville [12]
	[% mass]	[% mass]
CaO	58.10–68.00	43.12–85.22
SiO_2	18.4–24.5	13.84–28.44
Al_2O_3	3.10–5.04	3.15–7.80
Fe_2O_3	0.16–5.78	2–4
SO_3	0–5.35	1.5–2

Table 8
The oxide and mineral compositions of all OPCs considered in this study, from [8] and [9].

Oxide	OPC 1	OPC 2	OPC 3	OPC 4
	[%mass]	[%mass]	[%mass]	[%mass]
CaO	62.38	61.33	63.58	62.10
SiO_2	18.89	18.43	21.26	19.90
Al_2O_3	5.51	5.36	4.09	5.30
Fe_2O_3	2.55	2.64	2.89	2.80
SO_3	4.12	4.43	2.79	3.50
RO	5.53	5.37	4.40	4.09
LOI	1.02	2.44	0.99	2.31
C_3S	58.00	57.23	57.63	51.95
C_2S	10.50	9.76	17.60	18.01
C_3A	10.26	9.71	5.93	9.27
C_4AF	7.72	8.00	8.74	8.47
$C\overline{S}$	6.99	7.52	4.73	5.93

hydration; in the case of external chlorides, a smaller amount of chloroaluminates is formed, and these may dissociate under certain circumstances, releasing chloride ions in order to replenish those removed from the pore water by transport mechanisms. This approach suggested that more insights into the chloride binding ability of the AFm phase are needed in order to explain these observations.

Even though AFm is usually considered in cement literature to be only one phase, this generalization cannot be used when studying the microstructure of the cement paste. The AFm family consists of a great number of compounds, the most important being monosulfate (SO_4-AFm, $C_3A{\cdot}CaSO_4{\cdot}14H_2O$), hydroxy-AFm (HO-AFm, $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$) and monocarbonate ($C_3A{\cdot}CaCO_3{\cdot}10H_2O$). Moreover, intermediary compounds and solid solutions can form between these end-products. The carbonated AFm phases (monocarbonate, hemicarbonate and any of their solid solutions) will not be considered further. As stated in Section 2, the cement pastes studied are considered not to be carbonated.

There are a number of different mechanisms proposed in literature for the chemical conversion of AFm phases to Friedel's salt or Kuzel salt ($C_3A{\cdot}1/2CaCl_2{\cdot}1/2CaSO_4{\cdot}10H_2O$). These include the ion exchange mechanism [5,23] and the dissolution and precipitation mechanism [23]. Regardless of the proposed mechanism, binding isotherms are always used to evaluate the chloride binding capacity of various AFm phases (monosulfate, hydroxy-AFm).

The chloride ion is able to substitute the sulfate or hydroxyl groups in the structure of different AFm-type compounds, forming chloride-containing phases, Friedel's salt and Kuzel salt among other possible compositions with a varying degree of anion substitution by the chloride ions. Different solid solutions can occur between these compounds and chloride-free AFm compounds.

Despite the wide range of compositions of the AFm family, the difference in their chloride binding ability has never been detailed and quantified. Excepting the case of carbonated AFm phases, as well as the formation of solid solutions between various members, an important distinction can still be made. Henceforth, the chloride binding abilities of monosulfate and hydroxy-AFm will be distinguished from each other.

Table 9
Composition of all hardened cement pastes selected from [8] and [9]. Cement compositions OPC 1 ÷ OPC 4 are described in Table 8.

	Type of cement	w_0/b_0	Age at time of immersion (weeks)	m_{spl} (g)	α	α_F	β_F
HCP1	OPC 1	0.5	8	113.26	0.8	11.11	0.37
HCP2	OPC 2	0.5	8	110.87	0.8	9.37	0.39
HCP3	OPC 3	0.3	8	113.79	0.75	7.60	0.31
HCP4	OPC 3	0.5	8	114.70	0.8	8.20	0.26
HCP5	OPC 3	0.7	8	115.62	0.85	8.43	0.29
HCP6	OPC 4	0.4	6	109.55	0.58	8.03	0.28
HCP7	OPC 4	0.6	6	110.87	0.66	9.50	0.37
HCP8	OPC 4	0.8	6	111.03	0.67	10.32	0.40

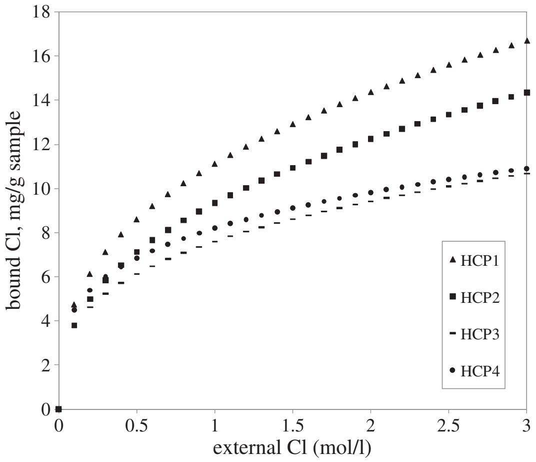

Fig. 1. Experimental binding isotherms of cement paste samples (11% rh) for compositions HCP1÷HCP4 (see Table 9), from [8].

Hirao et al. [25] have studied the chloride binding capacity of AFm, obtained from the hydration of C_3A in the presence of gypsum, in a ratio of C_3A:gypsum:water = 1:1:5. Given these synthesis conditions, only the formation of monosulfate can be expected because of the high gypsum content of the mix. The chloride binding capacity of this compound was found to obey a Freundlich-type isotherm, for the whole range of external chloride concentrations (up to over 4 M). The formation of Friedel's salt was clearly shown by XRD measurements, and the chloride binding isotherm was corrected by the amount of Friedel's salt determined by DSC measurements. An uncertainty in these measurements is mentioned for free chloride concentrations under 1 M, because of the formation of the monosulfate-Friedel's salt solid solution with undetermined proportions of sulfate and chloride ions.

Birnin-Yauri and Glasser [27] synthesized hydroxy-AFm—Friedel's salt solid solutions of different compositions, with the general formula $C_3A{\cdot}(1-x)CaCl_2{\cdot}xCa(OH)_2{\cdot}10H_2O$, where x satisfies the condition $0 \le x \le 0.9$. Birnin-Yauri and Glasser [27] concluded that intruding chlorides can react with the chloride-free AFm in the hardened cement paste. In the case of hydroxy-AFm, the reaction with intruding chlorides is considered to begin at ~2 mM [Cl^-]. Buffering is considered to be provided by the AFm, through changes in composition in order to incorporate chlorides

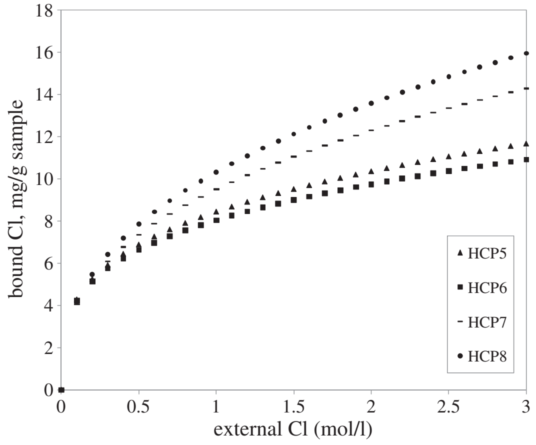

Fig. 2. Experimental binding isotherms of cement paste samples (11% rh) for compositions HCP5÷HCP8 (see Table 9), from [8] and [9].

in its structure. The buffering is considered to be exhausted above ~14.5 mM, at which point the AFm phase is virtually pure Friedel's salt.

A more recent article [32] brings new insights into the interactions between various AFm phases: HO-AFm, monosulfate, monocarbonate and Friedel's salt. Only the carbonate-free system will be discussed here, as explained above. In [32], chloride is introduced through intermixing of the phases (and not from an external solution) and the used compound is $CaCl_2$ and not NaCl. Differences between intermixed and external chlorides, as well as the effect of the associated cation were discussed in Section 1. However, the findings are in good agreement with other literature reviews [8,19,25]. The chloride ions are found to displace sulfate from a SO_4-AFm – HO-AFm solid solution, with the formation of Kuzel's salt for low $CaCl_2$ concentrations and Friedel's salt for higher concentrations, both in solid solution with HO-AFm. The sulfate ions which are thus released from monosulfate will form additional ettringite. This assumption will be incorporated in Section 5.2. When considering the chloride binding capacity of a commercial Portland cement, it is concluded in [32] that Friedel's salt is the only hydrated phase formed that incorporated chlorides into its structure, up to an external chloride concentration of 3 M. This is the assumption on which also the model in the title study will be based.

The difference between the chloride binding abilities of monosulfate and hydroxy-AFm, as summarized above, will be quantified in Section 5.1.

4.2. The role of ettringite, portlandite and Friedel's salt in chloride binding

Ekolu et al. [16] concluded that at intermediate levels of chloride concentrations (including 0.5 M NaCl) monosulfate is destroyed while most ettringite ($C_3A \cdot 3CaSO_4 \cdot 36H_2O$, the AFt phase) remains stable and that at high chloride levels both monosulfate and ettringite are destroyed with the release of Friedel's salt and gypsum as main final products. Birnin-Yauri and Glasser [27] propose that ettringite may play a role in chloride binding, even at lower free chloride concentrations, but this assumption is not sustained by any experimental data. However, Hirao et al. [25] experimentally tested the chloride binding capacity of the AFt phase and found that ettringite does not bind any chloride ions from an external solution. Elakneswaran et al. [26] consider the chloride binding capacity of ettringite to be intermediary between the one of Friedel's salt and the one of C-S-H, which is a very low binding capacity. In this case, AFt is considered to bind chlorides not through a chemical process, but through physical adsorption on the hydrate's surface. Moreover, due to the small amounts of ettringite formed in the cement paste, when compared to the one of C-S-H, the effect of the chloride adsorption on the surface of ettringite would be minimal. Still, considering the findings of Baloni et al. [32], that the ettringite amount formed increases because of the release of sulfate ions from monosulfate, the chloride binding ability of ettringite will also be estimated in Section 5.2.

Elakneswaran et al. [26] also give chloride binding isotherms of portlandite (CH) and Friedel's salt, proposing that Friedel's salt can, in its turn, adsorb chloride ions on its surface. Portlandite is believed to behave in the same way. It is stated that the dissociation processes of both Friedel's salt and portlandite give positive surfaces. According to the same study, Friedel's salt dissociates in water and its surface charge (which is due to $[Ca_2Al(OH)_6]^+$ groups) is compensated by chloride ions in the solution. Chlorides can also be adsorbed on the positive surface of dissociated portlandite and form CaOHCl, its crystal structure being detectable by XRD. However, Hirao et al. [25] measured the chloride binding capacity of CH and found that it does not bind chloride ions.

4.3. The chloride binding ability of the C-S-H phase

The surface of the C-S-H gel is known to be negatively charged, because the charges of the bridging silica tetrahedra are not always compensated [26,38]. This observation leads to applying the electrical double layer (EDL) theory, in order to explain the adsorption capacity of different ions of the C-S-H surface [26,39]. This theory had become more and more complex [40–44], allowing for the existence of three electrically charged layers, interfacial regions, and taking into consideration the size of the ions and their distance from the surface of the solid. Henocq [39] explains the adsorption of chloride ions on the surface of C-S-H by applying the model of the triple layer described by Stern [43] and Grahame [44] to the interface C-S-H/pore solution [45]. Based on the interpretation of electrokinetic potential curves, a structure made of a condensed layer of Na^+ ions on the surface, compensated partly by SiO^- groups and partly by an external layer made of hydroxyl ions (and chloride ions, in the presence of chlorides) was proposed. This external layer allows ionic exchanges with the solution. The adsorption of chloride ions can therefore be explained by an exchange mechanism between chloride ions from the pore solution and hydroxyl ions from the C-S-H layers. The OH^- ion is loosely bound, permitting the Cl^- ion to be substituted in the interlayer space and ensure the electroneutrality of the system [39]. This physical adsorption mechanism of chloride ions on the surface of the C-S-H gel explains the fact that C-S-H has a lower chloride binding ability than the AFm phase, which binds chlorides through chemical substitution (as discussed in Sections 4.1 and 4.2).

The EDL theory implies the influence of several factors over the chloride binding ability of the C-S-H gel, the most important of which are the C/S ratio of the gel, the composition and pH of the pore solution and associated cation of the chloride ion. As explained in Section 1, the only source of chloride ions considered in this study is NaCl. A usual pH is assumed for the pore solution (12.5–13.4, according to [1]) and a C/S ratio of 1.7 for the C-S-H gel [30]. Moreover, the C-S-H gel and the pore solution are considered to be homogenous in composition throughout a hardened paste in equilibrium with its surrounding solution. Therefore, all C-S-H should have the same chloride binding ability, regardless of its source (C_3S or C_2S) and the pore solution is considered to have a constant pH throughout the sample.

5. Chloride binding isotherms related to binder composition and hydration products

All chloride binding isotherms in the following sections will be termed either $C^0_{b,hp}$ for chloride binding capacities expressed in mg Cl/g hydration product conditioned to 11% rh [8,25,26], or $C_{b,hp}$ for the chloride binding capacities expressed in mg Cl/ g sample at 11% rh (as calculated from [8,9,25]). The molar mass of each hydration product can be found in Table 3 and has already been incorporated in the following isotherm expressions where so needed. The term m_{hp} refers to the mass of the specified hydration product, in grams, calculated using Table 3. The mass of sample in grams at 11% rh, m_{spl}, is always computed according to Eq. (6). Eq. (7) gives the general relation between $C^0_{b,hp}$ and $C_{b,hp}$:

$$C_{b,hp} = C^0_{b,hp} \times \frac{m_{hp}}{m_{spl}}. \tag{7}$$

The chloride concentration of the external solution, c, is always expressed in mol Cl/l solution.

5.1. The chloride binding capacity of the AFm phase

Hirao et al. [25] studied the chloride binding of the pure AFm phase, as described in Section 4. They have found the following

Freundlich-type isotherm which describes chloride binding by the monosulfate phase, in mg Cl/ g monosulfate:

$$C^0_{b,SO_4-AFm} = 51.89c^{0.58}. \tag{8}$$

As mentioned in Section 4, Birnin-Yauri and Glasser [27] consider that 100% of the quantity of HO-AFm is completely transformed into Friedel's salt at a free chlorides concentration greater than 0.015 mol/L. Considering the fact that one mole of hydroxy-AFm binds two moles of chloride ions in order to form Friedel's salt, and using the molecular masses from Table 3, the amount of chloride which can be bound by C_4AH_{13}, in mg Cl/ g HO-AFm becomes:

$$C^0_{b,HO-AFm} = 126.5 \tag{9}$$

constant for external chloride concentrations over 0.015 M.

The sum of Eqs. (8) and (9) will be used henceforth to compute the total binding capacity of the AFm phase.

5.2. The chloride binding capacity of the C-S-H phase

Zibara [8] also determined the chloride binding ability of the hydration products of pure C_3S and C_2S in mg Cl/ g C-S-H gel formed, compensating for the amount of CH formed, because it is considered not to bind chlorides:

$$C^0_{b,C_3S} = 6.65c^{0.334} \tag{10}$$

$$C^0_{b,C_2S} = 7.89c^{0.136}. \tag{11}$$

Even though their coefficients are quite different, the isotherms defined by Eqs. (10) and (11) show almost the same behavior for the C_3S and C_2S phases when the amount of C-S-H generated is taken into account. A combination of these isotherms that takes into account the C_3S:C_2S ratio of the cement will be used throughout this study. In order to combine these isotherms into one equation, the mass fraction of C_3S (δ_{C3S}) and C_2S (δ_{C2S}) in their sum will be used:

$$\delta_{C_3S} = \frac{m_{C_3S}}{m_{C_3S} + m_{C_2S}} \tag{12}$$

$$\delta_{C_2S} = \frac{m_{C_2S}}{m_{C_3S} + m_{C_2S}} = 1 - \delta_{C_3S}. \tag{13}$$

Eq. (14) describes the chloride binding capacity of the C-S-H phase in mg Cl/g C-S-H, as it will be computed in all following results and termed $C_{b,C-S-H,Z}$.

$$C^0_{b,C-S-H,Z} = \left(6.65c^{0.334}\cdot\delta_{C_3S} + 7.89c^{0.136}\cdot\delta_{C_2S}\right). \tag{14}$$

Hirao et al. [25] experimentally determined a Langmuir-type isotherm for the chloride binding of the C-S-H phase, in mg Cl/g C-S-H gel conditioned at 11% rh:

$$C^0_{b,C-S-H,H} = 21.84\cdot\frac{2.65c}{1+2.65c}. \tag{15}$$

Elakneswaran et al. [26] also propose a chloride binding isotherm for the C-S-H phase in mg Cl/g $C_{1.7}SH_{2.1}$, which has been fitted to the following Freundlich isotherm, termed $C_{b,C-S-H,E}$:

$$C^0_{b,C-S-H,E} = 12c^{0.63}. \tag{16}$$

Fig. 3 shows isotherms C^0_{b,SO_4-AFm} (Eq. (8)), $C^0_{b,HO-AFm}$ (Eq. (9)), $C^0_{b,C-S-H,Z}$ (Eq. (14)), $C^0_{b,C-S-H,H}$ (Eq. (15)) and $C^0_{b,C-S-H,E}$ (Eq. (16)), describing the chloride binding ability of monosulfate, hydroxy-AFm and respectively C-S-H according to [8,25,26], in mg Cl/g hydrated phase. Fig. 4 shows the isotherms C_{b,SO_4-AFm}, $C_{b,HO-AFm}$, $C_{b,C-S-H,Z}$, $C_{b,C-S-H,H}$ and $C_{b,C-S-H,E}$ applied to HCP2 using Eq. (7), and so taking into consideration the relative amount of each hydrate in the cement paste.

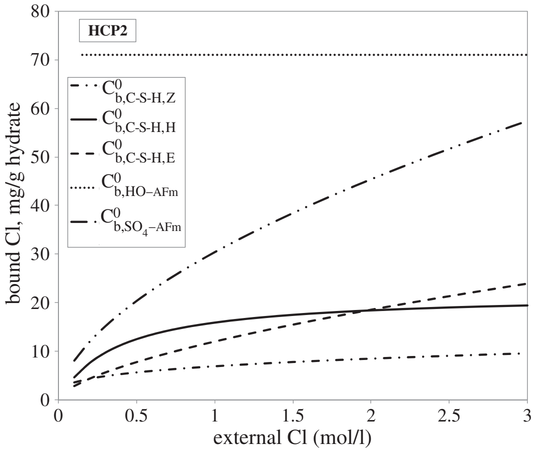

Fig. 3. Isotherms (10), (11), (16), (17) and (18) describing the chloride binding ability of hydroxy-AFm, monosulfate and respectively C-S-H at 11% rh, according to [8,25–27]. The composition of paste HCP2 can be found in Table 9.

The difference between the $C^0_{b,C-S-H,H}$, $C^0_{b,C-S-H,E}$ and $C^0_{b,C-S-H,Z}$ isotherms can have multiple explanations. The quantitative effects of a number of influencing factors cannot be precisely asserted. The first factor that needs to be considered is the very large w_0/b_0 (10:1) ratio employed in [25], which will not be found in any real concrete structure, as opposed to the w_0/b_0 of 0.5 employed in [8]. Also, the fact that in [25] the solid and liquid fractions of the sample were separated by suction filtering and not by drying using acetone leads to the conclusion that the chloride amounts that can be bound by the gel water of the C-S-H, when fully rehydrated in chloride solution, were also included in the measurement. Furthermore, a small fraction (evaluated as ≤5%) of the free chlorides that entered the capillary space upon rehydration could still be present at the time of the chloride content measurement. In the case of the binding isotherm $C_{b,C-S-H,E}$ determined in [26], the results were deduced from the isotherms of HCP and portlandite. The phase assemblage was predicted using a speciation software, and corrected for the chemically bound chlorides determined through XRD measurements. The maximum external chloride concentration used in these experiments was 1 M. However, at such low concentrations, the results given by XRD are not conclusive, as explained in Section 4.1. Conversely, Zibara [8] measured the chloride binding of hydrating C_3S and C_2S pastes with a w_0/b_0 of 0.5 with NaOH and KOH additions to mimic the control solution. The obtained values were corrected for the amount of CH formed, using the paste model detailed in Section 2.

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 all eight considered 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 the C-S-H chloride binding isotherm (15) proposed by Hirao et al. [25], $C_{b,H}$ is computed as its sum with Eqs. (8) and (9). In the same way, $C_{b,Z}$, the sum of Eq. (14) with Eqs. (8) and (9) can be calculated. Last, using Eq. (16), Eqs. (8) and (9), the sum of the C-S-H isotherm proposed by Elakneswaran et al. [26] and the isotherm of AFm, termed $C_{b,E}$, is computed. Fig. 5 compares these three composed isotherms with the experimentally determined values for the composition of HCP6 as an example. The $C_{b,E}$ isotherm is the poorest fit in

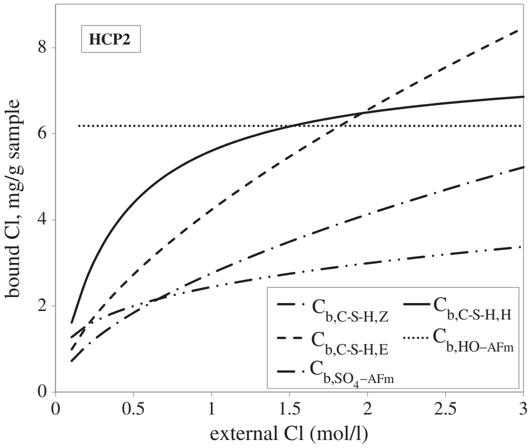

Fig. 4. Isotherms (10), (11), (16), (17) and (18) applied to HCP2 (Table 9) using Eq. (9), and so taking into consideration the relative amount of each hydrate in the cement paste.

terms of its shape when compared to the experimental data. Moreover, its relative error starts at 50% and increases with the increase of the external chlorides concentration. Therefore, this isotherm does not satisfactorily describe the chloride binding capacity of C-S-H. In terms of the shape of the curve, the $C_{b,H}$ isotherm is closest to the experimental data. However, it can be seen that, again, its predicted values are 50% higher than the experimentally obtained data. The $C_{b,Z}$ isotherm has the lowest relative errors and standard deviations from experimental results, when compared to the $C_{b,H}$ and $C_{b,E}$ isotherms, even if the shape of the curve is not the best fit. The higher predicted values for the lower range of external chlorides can be attributed to the assumption that all HO-AFm is already transformed into Friedel's salt, which might not be completely accurate for all cement pastes. Given these data, the $C^0_{b,C-S-H,Z}$ isotherm (Eq. (14)) is chosen as the best to describe the chloride binding capacity of the C-S-H phase. The isotherm $C_{b,Z}$ will be referred to as "the basic model" henceforth. An "extended model" will now be presented, in order to include the chloride binding abilities of other hydrated phases in an OPC paste. The contributions of these phases are not as significant as the ones of AFm and C-S-H, but their addition shows a positive effect on the results of the new chloride binding model.

5.3. Chloride binding abilities of other OPC hydrates: the extended model

The other hydrated phases that are considered in literature to be able to bind chlorides are portlandite, Friedel's salt and ettringite, as discussed in Section 4.2. Elakneswaran et al. [26] have obtained chloride sorption isotherms of portlandite and Friedel's salt. Eqs. (17) and (18) describe the sorption capacity of portlandite and Friedel's salt, in mg Cl/g portlandite and mg Cl/g FS respectively, for free chloride concentrations under one mol/L:

$$C^0_{b,\,CH} = 0.087 \cdot c^{0.62} \tag{17}$$

$$C^0_{b,\,FS} = 0.31 \cdot c^{0.46}. \tag{18}$$

The mass m_{FS} is computed for Friedel's salt at 11% rh, $C_3A \cdot CaCl_2 \cdot 6H_2O$, with the molar mass of 489.27 g/mol:

$$m_{FS} = 6.9 \cdot \left(C_{b,\,C_4A\bar{S}H_{10}} + C_{b,\,C_4AH_{13}}\right). \tag{19}$$

Ettringite is also mentioned in [26], and believed to give a chloride sorption capacity lower than portlandite and Friedel's salt, but higher than tobermorite. The amount of AFt increases with the intrusion of chloride ions and the formation of Friedel's salt (see Section 4.2.), so this contribution needs to be taken into account. In order to do this, the first assumption is that ettringite has the same chloride binding ability as tobermorite (which is estimated in Eq. (10)), so that its minimum influence can be assessed. Then, the amount of newly formed ettringite, m_{ettr}, needs to be estimated from the amount of Friedel's salt (Eq. (18)), using the molecular mass of AFt from Table 3 and the initial ettringite amount formed before the intrusion of chlorides, from Table 5:

$$C_{b,AFt} = C^0_{b,C_2S} \cdot \frac{m_{ettr}}{m_{spl}} = 6.65 \cdot c^{0.334} \cdot \frac{m_{C_6A\bar{S}_3H_{12}} + 0.3 \cdot m_{FS}}{m_{spl}}. \tag{20}$$

Isotherms incorporating the contribution of portlandite, ettringite, Friedel's salt and all the possible combinations between them were constructed by adding the contribution of the respective phases to the $C_{b,Z}$ isotherm.

The influence of adding the binding capacity of portlandite or Friedel's salt alone is beneficial, even though very low, for all cases considered (compositions from Tables 8 and 9). Adding the contribution of the AFt phase does not improve the precision of the model, its influence being also very low, but either positive or negative for the considered hardened cement pastes. The combined effect of two of these phases, or all three together, is beneficial in most, but not all cases. However, since these effects are extremely low (with contributions usually well under 1% of the total bound chlorides), they should only be taken into account for theoretical models with precise phase assemblages. For practical cases in which a high precision is not needed, the use of the basic model is recommended.

For the rest of this study, the total bound chlorides for all considered samples will be calculated using the isotherm $C_{b,\,Z,\,CH,\,FS}$, defined as the sum of Eqs. (8), (9), (14), (17) and (18) and termed from now on C_b. This extended model offers the best precision in predicting the chloride binding ability of hardened OPC pastes by incorporating the chloride binding abilities of both Friedel's salt and portlandite.

6. Comparison with other models from literature

Zibara [8] has proposed two expressions for the α_F coefficient of a Freundlich isotherm describing the chloride binding capacity of a hardened cement paste:

$$\alpha_F = 0.86x_{C_3A} + 0.44x_{C_4AF} + 0.16\left(x_{C_2S} + x_{C_3S}\right) - 12.44 \tag{21}$$

$$\alpha_F = 0.65x_{C_3A} + 0.24x_{C_4AF} - 0.35x_{SO_3} + 3.38 \tag{22}$$

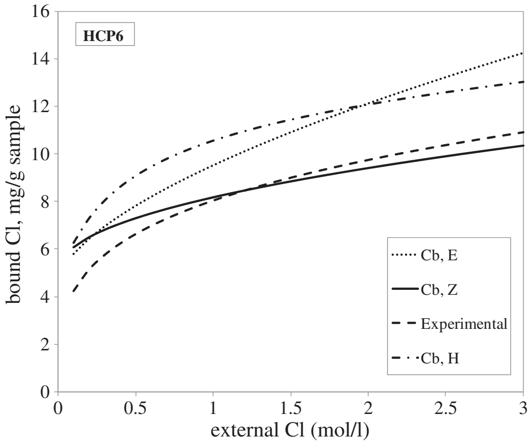

Fig. 5. Comparison between $C_{b,Z}$, $C_{b,H}$ and $C_{b,E}$ and the experimental data from [8], for composition HCP6 (Table 9).

and one expression for the β_F exponent of the same isotherm:

$$\beta_F = 0.003\cdot x_{C_3A} + 0.005\cdot x_{C_4AF} + 0.019\cdot x_{SO_3} + 0.23. \qquad (23)$$

These coefficients depend on the composition of the considered cement (% mass of clinker minerals and % mass of SO_3). Eqs. (21)–(23) have been obtained by fitting experimental data to a number of cement compositions, without taking into account the water to binder ratio or age of the sample. Moreover, these fitted equations do not take into account the formed hydration products and have no physical or chemical basis for their predictions.

Based on Eqs. (8) and (15), Hirao et al. [25] estimated the total chloride binding capacity of a cement paste as:

$$C_{b,H} = 0.62\cdot\frac{2.65c}{1+2.65c}\cdot x_{CSH} + 1.38c^{0.58}\cdot x_{AFm} \qquad (24)$$

where $x_{C\text{-}S\text{-}H}$ and x_{AFm} should be calculated according to a method published by the Japan Concrete Institute. In this study, the $x_{C\text{-}S\text{-}H}$ and x_{AFm} quantities will be predicted using the paste model described in Section 2.

Fig. 6 is an example applied on HCP6 and it shows the isotherms obtained using Eqs. (22) and (23), termed “Zibara” and Eq. (24), termed “Hirao”, and compares them to the experimental results and to the chloride binding C_b predicted using the new extended model. The use of either Eq. (21) or (22) when computing the “Zibara” isotherm will render almost identical results, so the choice is not influencing the presented values. Fig. 7 compares the chloride binding capacity of each hydrated paste (compositions from Tables 8 and 9) with the experimental values at a free chloride concentration of 2 M, as the regular value for the RCM test. It can be seen from both Figs. 6 and 7 that the proposed isotherm C_b is a very good fit for the considered experimental results.

The highest drawback of the Zibara model [8] is that it predicts the same amount of bound chlorides for OPC pastes obtained from the same cement but with different w_0/b_0 ratios and curing ages; in other words, that it is based only on a fit on cement composition and does not take into account other mixing and curing parameters. Therefore, that model predicts the same chloride binding capacity for pastes HCP3 ÷ HCP5, even though the authors have measured different values for each sample during the performed laboratory experiments.

Applying the hydration model described in Section 2 [29,30,47] to the model of Hirao et al. [25], the latter is found to perform well. In such conditions, the currently proposed model and the Hirao model [25] are compatible, and in good agreement with experiments. However, this hydration model assumes all AFm to consist of only one compound and does not make the distinction between the different chloride binding capacities of the AFm members, as the newly proposed model does. The importance of this distinction will be further pointed out in Section 7.

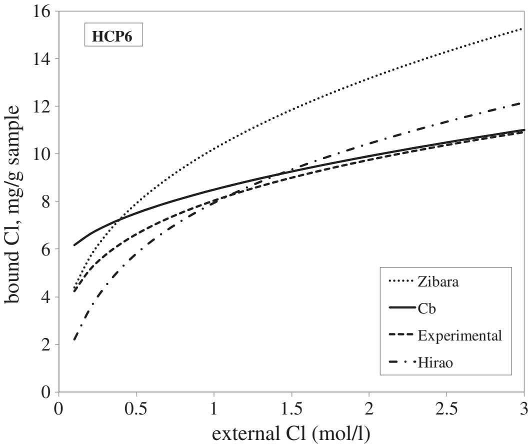

Fig. 6. Comparison between the proposed model, the models of Hirao et al. [25] and Zibara [8], and the experimental data from [9], for composition HCP6 (see Table 9).

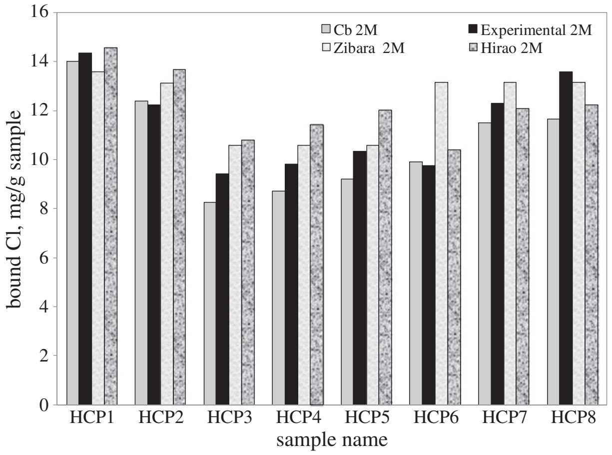

Fig. 7. The chloride binding capacity of each hydrated paste (see Table 9) with the experimental values at a free chloride concentration of 2 M.

7. Summary and 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 hydration. The chloride binding of several hydrated phases (C-S-H, monosulfate, hydroxy-AFm, AFt, CH, and Friedel's salt) have been studied and estimated in relation to the chloride content of the pore solution.

Based on an extensive analysis of experimental data found in literature, a new chloride binding isotherm for the AFm phase is given. This formula takes into account the different chloride binding abilities of monosulfate and hydroxy-AFm. This difference between the chloride binding abilities of various members of the AFm family has not been taken into consideration in any other model, even though it is significant and its inclusion can change the results greatly. Using the new AFm isotherm and several sets of experimental chloride binding isotherms from literature, a new formula for estimating the chloride adsorption capacity of the C-S-H phase is proposed.

Combining the two new isotherms, 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. This isotherm has been termed the “basic model”. When compared to experimental data, the results obtained using this new chloride binding isotherm have proven to accurately describe the chloride binding capacity of OPC pastes, results being within 8% of the experimental values for the whole range of free chloride concentrations considered, of up to 3 M. An “extended model” was also developed, in order to assess the contribution of portlandite, ettringite and the newly formed Friedel's salt. Adding the contributions of either of these phases has a positive influence on the precision of the model, but their estimation requires a clear understanding of the phase assemblage of a given paste. The addition of the contributions of both Friedel's salt and portlandite was found to be the most beneficial over the range of compositions of hardened cement pastes considered.

This new model is based on the chloride binding abilities of each hydrated phase, and therefore can distinguish between their contributions at different free chloride concentrations. The contribution of HO-AFm is the greatest for all free chloride concentrations, but its importance decreases with the increase in free chlorides (from 60% at 0.3 M external chlorides, to 30% at 3 M), as all HO-AFm is considered to be transformed to Friedel's salt for external chloride concentrations of at least 0.015 M. The contribution of monosulfate does not equal the one of HO-AFm until high chloride concentrations, but it increases with the increase in free chlorides, from 13% at 0.3 M external chlorides concentration, to over 33% of the total chloride binding capacity. The contribution of the AFm phases amounts to ~70% of the total chloride binding capacity of a cement paste, which is in line with the conclusions of [32], which state that Friedel's salt traps the most chlorides on a mass basis.

The contribution of C-S-H is the one which remains fairly constant for the whole range of external chloride concentrations, between 25% and 28%. The lowest contributions are the ones of portlandite and Friedel's salt, whose sum amounts to only 2–5% of the total bound chlorides in an OPC paste. At an external chlorides concentration of 0.6 M (usual for sea water), the total chloride binding capacity of an OPC paste can be divided between the hydrated products as: 49% to HO-AFm, 20% to SO_4-AFm, 28% to C-S-H and 3% to portlandite and Friedel's salt. For higher concentrations this balance will change in favor of the monosulfate contribution. For example, at an external chlorides concentration of 2 M, the following contributions of the hydrated phases were calculated: 37% to HO-AFm, 30% to SO_4-AFm, 28.5% to C-S-H and 4.5% to portlandite and Friedel's salt. It can be concluded that, at lower concentrations, a high content in C_3A is beneficial for the ability of an OPC paste to bind chlorides, while at higher external chloride concentrations (for instance in salty lakes), the content in sulfates also becomes important.

Further research will include extending the present model to slag blended cements, taking into consideration their different hydration products and phase assemblages.

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