Chloride binding isotherms of various cements basing on binding capacity of hydrates

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Abstract. This study investigated the chloride binding isotherms of various cement types, especially the contributions of C-S-H and AFm hydrates to the chloride binding isotherms were determined. Ordinary Portland cement (OPC), Modified cement (MC), Rapid-hardening Portland cement (RHC) and Low-heat Portland cement (LHC) were used. The total chloride contents and free chloride contents were analyzed by ASTM. The contents of C-S-H, AFm hydrates and Friedel's salt were determined by X-ray diffraction Rietveld (XRD Rietveld) analysis. The results showed that OPC had the highest chloride binding capacity, and, LHC had the lowest binding capacity of chloride ions. MC and RHC had very similar capacities to bind chloride ions. Experimental equations which distinguish the chemically bound chloride and physically bound chloride were formulated to determine amounts of the bound chloride basing on chloride binding capacity of hydrates.

Keywords: chloride binding isotherm; C-S-H; AFm; Friedel's salt; cement types

1. Introduction

Chloride-induced corrosion of reinforcement of concrete structures in marine environments is a major concern in marine construction. The chloride involved in this corrosion is present in concrete both in free or uncombined form as well as bound to cement hydration products through adsorption of C-S-H or in the chemical composition in the form of Friedel's salt $(C_3A.CaCl_2.10H_2O)$. Generally, free chloride is considered to be responsible for the initiation of corrosion, and also that only free chloride can penetrate deeper inside the concrete cover through solution to reach the steel surface. Therefore, the binding of chloride retards the penetration process which delays the time when corrosion starts. As a result, it is necessary to consider chloride binding capacity of cement in models to predict chloride penetration into concrete structures. Many models have been proposed to evaluate the contents of free and bound chloride, these models were based on experimental analysis of free and bound chloride and showed linear,

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Langmuir, or Freundlich isotherms (Paul *et al*. 1999, Neilsen *et al*. 2005 and Rui *et al*. 2003). However, the models are still limited when applied to all commonly used cement types, and also, they do not specify clearly the various contributions of the physically bound chloride absorbed by C-S-H gel, or the chemically bound chloride which is present in the solid phase of Friedel's salt due to the reaction of AFm with chloride ions, to the complete chloride binding isotherms of cement types. The major hydrates of cement paste are C-S-H gel, $Ca(OH)_2$, AFt ($C_3A.3CaSO_4.32H_2O$), and AFm ($C_3A.3CaSO_4.10H_2O$). Of these hydrates, AFt and $Ca(OH)_2$ has little capacity to bind chloride (Hirao *et al*. 2005); C-S-H has a very large surface and is able to bind various kinds of ions (Tran *et al*. 2009 and Tang 1993) including chloride ions. Further, the chloride binding capacity of C-S-H depends on the chemical composition and surface area as well as the kind of chloride solution and experimental conditions (Johannesson *et al*. 2007). Suryavanshi *et al*. 1996 found that Friedel's salt formed by two separate mechanisms, an adsorption mechanism and an anion-exchange mechanism. The anion-exchange mechanism was also reported to form Friedel's salt (Hirao *et al*. 2005 and Wang 2011). The chloride binding capacity of AFm is higher than that of the C-S-H gel, however, C-S-H gel comprises most of concrete, maybe up to 70% of the mass of cement paste. Hence, overall, the physically bound chloride amount due to the absorption of chloride ions on C-S-H is much higher than that of the chemically bound chloride (Tang 1993 and Glass 2000). Various types of cement with different compound compositions produce different amounts of hydrates. Consequently, the chloride binding isotherms of cement may vary depending on the types of cement. In general, the chloride binding isotherm of cement is determined by changing the concentration of chlorides at the same water cement ratio (W/C). On the other hand, the chloride diffusion coefficient is dependent on the water cement ratio. This implied that the chloride binding isotherms of cement is influenced by the water cement ratio.

In this study, the chloride binding isotherms of various cement types were estimated by varying W/C at the same concentration of chlorides. Further, the contributions of the cement hydrates such as C-S-H gel and AFm to the whole chloride binding isotherm also were investigated.

2. Experiments

2.1 Materials and mix proportions

Four different types of cements were used in this study; ordinary Portland cement (OPC), moderate heat Portland cement (MC), raid high strength Portland cement (RHC), and low heat Portland cement (LHC). The chemical and physical properties and mineral compositions of various cement types are given in Table 1 and 2, respectively. Deionized water was used as mixing water. Reagent grade sodium chloride and deionized water were used to prepare the sodium chloride solution. As shown in Table 3, in total 16 different cement pastes with different W/C ratios of 0.3, 0.4, 0.5 and 0.6 were prepared as specimens.

2.2 Experimental procedure

The mixing of cement paste was carried out by a high-speed mixer for three minutes. After mixing, the pastes are cast in steel cubic molds with 5 cm sides. The molds were sealed and kept in a chamber at a constant temperature of $22^°C$ for 24 hours. Then, specimens were demolded and

Table 1 The chmical compositions and physical properties of various cement types

Cement	Chemical compositions (% by mass)							Density	Blaine surface	Ignition
type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Cl	(g/cm^3)	area (cm^2/g)	loss (%)
OPC	21.66	5.58	2.79	63.92	2.55	2.32	-	3.17	3500	0.72
MC	23.31	3.96	4.32	63.59	0.26	2.52	0.012	3.21	3090	0.77
RHC	20.30	4.66	2.63	64.70	1.91	3.06	0.006	3.15	4660	0.54
LHC	25.85	3.21	3.70	63.09	0.10	2.44	0.005	3.24	3330	0.81

Table 2 The mineral compositions of various cement types

Cement type	Mineral compositions (% by mass)			
	C_3S	C_2S	C_3A	C_4AF
OPC	58.3	22.6	6.4	10.1
MC	52.8	28.5	5.1	10.8
RHC	69.4	16.1	4.9	8.5
LHC	33.3	53.0	3.3	7.8

Table 3 The composition of mixtures

No	Mix series	Cement type	W/C
1	MI-1		0.3
2	MI-2	OPC – ASTM Type I	0.4
3	MI-3		0.5
4	MI-4		0.6
5	MII-1		0.3
6	MII-2		0.4
7	MII-3	MC – ASTM Type II	0.5
8	MII-4		0.6
9	MIII-1		0.3
10	MIII-2		0.4
11	MIII-3	RHC – ASTM Type III	0.5
12	MIII-4		0.6
13	MIV-1		0.3
14	MIV-2		0.4
15	MIV-3	LHC – ASTM Type IV	0.5
16	MIV-4		0.6

cured in a saturated lime condition for 28 days. After this, specimens were immersed in a 10% sodium chloride solution; for 1 month in the case of paste specimens with the W/C = 0.5 and 0.6 mixes, and 2 months in the case of paste specimens with W/C = 0.3 and 0.4, respectively. At the end of the immersion period, three samples with 1cm thick were sawn from the exposed surfaces, and the total chloride ions, C_t, and free chloride ions, C_f, in the specimens were determined with the procedures in ASTM C 1152 and ASTM C 1218 respectively.

For the tests of total chloride content – ASTM C1152, 10g of powder sample passing a 850 μm sieve is dispersed in a 250 ml beaker with 75 ml of deionized water, 25 ml of dilute (1+1) nitric acid added slowly, then 3 ml of hydrogen peroxide (30% solution), and 20 drops of acid nitric (1+1) added in excess, and heat the covered beaker rapidly to boiling. After removal of the beaker

from the hot plate and filtering the solution, the chloride concentration in the filtrate will be analyzed by ion chromatography. Experimental procedures of tests of the free chloride content – ASTM C1218 are very similar to those of the total chloride content test. However, only 50 ml of deionized water is used instead of 75 ml, and boiling of the solution in the beaker is for 5 min. Then left to stand for 24 h for filtering by gravity or suction through a fine-texture. Adding 3 ml of (1:1) nitric acid and 3 ml of hydrogen peroxide (30% solution) to the filtrate, covering the beaker with a watch glass and allow it to stand for 1 to 2 min. Then heating the covered beaker rapidly to boiling, and the chloride concentration in the filtrate will be also analyzed by ion chromatography.

The bound chloride content, C_b, is a difference between the total chloride content, C_t, and the free chloride content, C_f. In addition, X-ray diffraction (XRD) Rietveld analysis was performed to determine the degrees of hydration and hydrate contents of cement pastes; C-S-H, AFm and Friedel's salt. The chemically bound chloride content, C_{cb}, is calculated through Friedel's salt content which is analyzed by XRD Rietveld method. Finally, the physically bound chloride content, C_{pb}, is calculated by the difference between the bound chloride content, C_b, and the chemically bound chloride content, C_{cb}.

The XRD test was conducted by X-ray defractometer using Ni-filtered CuK_α operating at 40 kV and 20 mA. A range of $5°$ to $70°$ (2θ) was scanned at step intervals of 0.02^0 (2θ) using a step scan time of 1s and 2^0/s scan speeds. The divergence slit, scattering slit, and receiving slit were $1/2°$, $1/2°$, and 0.3 mm, respectively. To determine the amount of amorphous C-S-H in the cement pastes, corundum (α-Al_2O_3) was added to the paste sample as an internal reference with 10% by mass of the cement paste (Termkhajornkit *et al*. 2005). The corundum and cement paste were mixed in a ball mill at 100 rpm for three minutes. SIROQUANT version 3.0 was used as a Rietveld analysis software.

3. Results and discussion

3.1 Chloride binding isotherms of various cement types

Fig. 1 shows the relationship between the free chloride contents and the total chloride contents of various cement pastes made from different cement types. At the same chloride concentration and immersion period, the chloride binding capacity of cement which can be expressed by the difference between the total chloride and the free chloride contents varied by the cement types. The relationship between the free chloride content and the total chloride content can be formulated by a power approximation as follows:

$$\text{OPC:} \quad y = 1.3218x^{0.995}; R^2 = 0.997 \tag{1}$$

$$\text{MC:} \quad y = 1.0989x^{1.022}; R^2 = 0.996 \tag{2}$$

$$\text{RHC:} \quad y = 1.1695x^{0.9954}; R^2 = 0.993 \tag{3}$$

$$\text{LHC:} \quad y = 1.0987x^{0.9864}; R^2 = 0.996 \tag{4}$$

where, x is the free chloride (% by mass of cement) and y is the total chloride (% by mass of cement).
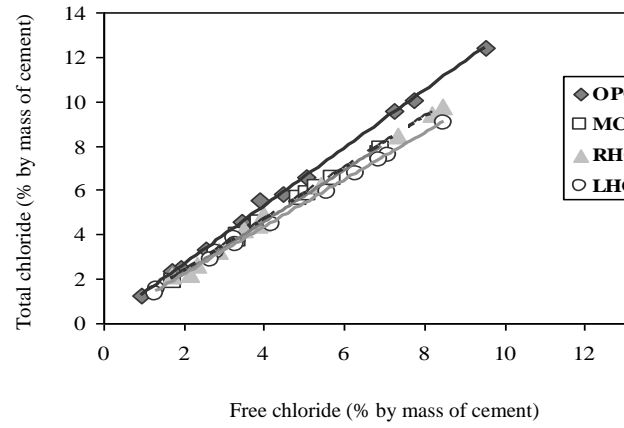
Fig. 1 Relationship between free chloride and total chloride of various cement types
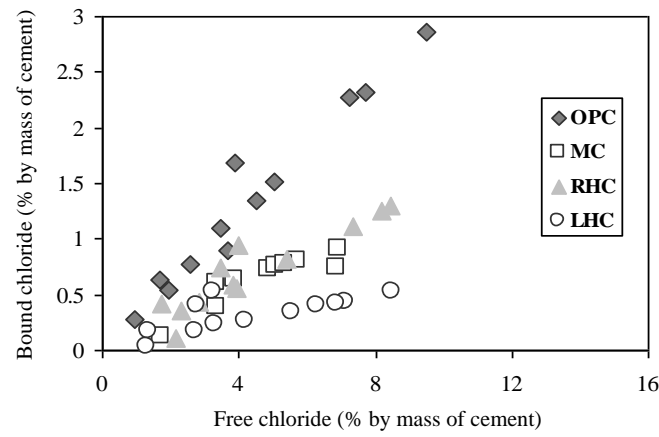
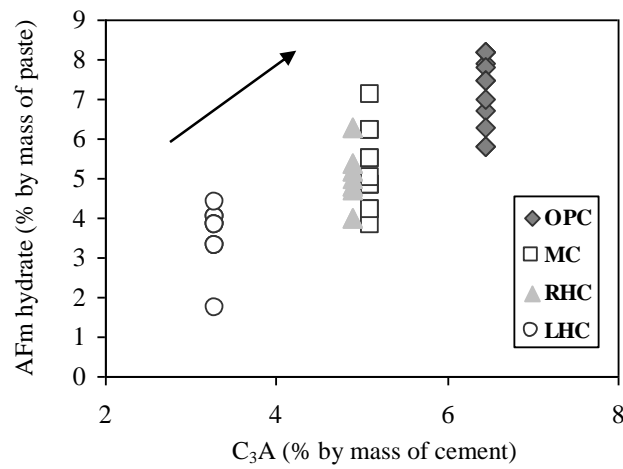Fig. 2 Chloride binding capacity of various cement types

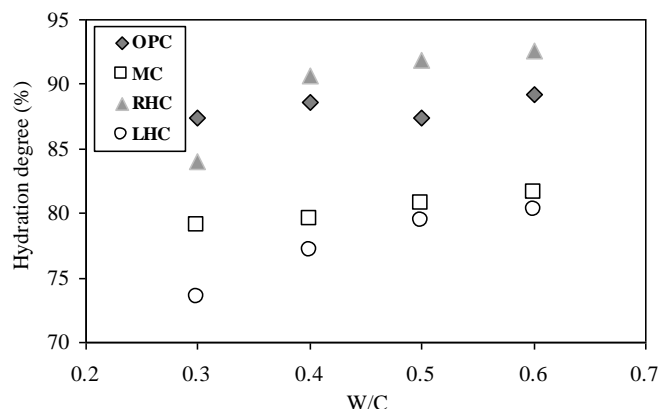Fig. 3 AFm hydrate contents with various C3A contents

Fig. 4 Hydration degree of cements with varying W/C

To be more specific, the bound chloride content, the physically bound chloride content and the chemically bound chloride content were analyzed detailed.

Hirao *et al*. 2005 reported that AFm reacts with chlorides to form Kuzel's salt and Friedel's salt at low concentration below 1 molar/liter and at high concentration more than 1 molar/liter, respectively. They also showed that AFt and $Ca(OH)_2$ have no chloride binding capacity. Moreover, the prepare C-S-H gel dose not react with chloride ions, but chloride ions still appear on the surface of C-S-H and at interlayers of C-S-H. This implies that chloride binding of C-S-H is mainly due to physical bonding force such as Van der Waals forces. And, chloride bound by C-S-H gel can be represented by Langmuir adsorption. From the previous study's results, in this study, the authors assume that the chemically bound chloride is present in the solid phase of Friedel's salt, while the physically bound chloride ions is adsorbed by C-S-H gel.

Fig. 2 shows the relationship between the bound chloride and the free chloride for pastes. All data for four different types of cement show similar trends; the amount of bound chloride increases consistently with increasing the free chloride content. However, it can be also confirmed that the chloride binding isotherm varied by the types of cement: The OPC paste everywhere has the highest ability to bind chloride ions, whereas LHC paste has the lowest capacity to bind chloride ions, and the chloride binding capacity of MC paste and RHC paste is very similar, showing the moderate capacity. As described in section 2.2, with a specific cement type, *w/c* changes as 0.3, 0.4, 0.5 and 0.6. Also, at the end of curing period, samples with 1cm thick were sawn from the hardened paste to account for contents of hydrates. The differences in cement compounds and its compositions result in differences in both the hydration degree of the cement, and the kind and amount of hydrates. Among of four cements, OPC with the highest C_3A content showed the highest product of Friedel's salt since the amount of AFm hydrate in paste before immersing in chloride solution is the highest among the four cements (Fig. 3).

Further, as shown in Fig. 4, OPC paste also had the second highest hydration degree. This implies that the quantity of C-S-H hydrate in OPC paste is enough to absorb more chloride ions. Additionally, LHC paste has the lowest C-S-H hydrate content since the hydration degree is the lowest due to the high content of C_2S compounds. All explanations described here answer the question why OPC paste has the highest capacity to bind chloride ion, while LHC paste has the lowest.

3.2 Contribution of physically and chemically bound chloride to the total chloride binding isotherms of various cement types

As mentioned in above section, it can be expected that the chlorides binding capacity of cement can be estimated mainly by chemically bound chloride due to Friedel's salt and the physically bound chloride due to C-S-H gel. It is difficult to qualify Friedel's salt in cement by XRD Rietveld analysis when the qualities of Friedel's salt is a little. On the other hand, AFm that is the major compound of paste reacts with chloride ions, producing Friedel's salt. The amount of AFm produced is large and can be quantified by XRD Rietveld analysis. Hence, in this study, the amount of Friedel's salt is estimated by the difference between the AFm hydrate content before immersing in chloride solution and the AFm hydrate content remaining at the end of the immersion period.

To be more specific, in this section, the relationship among the free chloride content, the chemically bound chloride content due to Friedel's salt and the physically bound chloride content due to C-S-H gel, and further the chloride binding isotherm for Friedel's salt and C-S-H gel were investigated.

Fig. 5 shows relationship between the free chloride content and the physically bound chloride content, while Fig. 6 presents relationship between the free chloride content and the chemically bound chloride content. From Fig. 5, the contents of the physically chloride at the same free chloride contents vary greatly with cement types: The order of chloride adsorption capacity from highest to lowest is OPC, RHC, MC and LHC. In general, the adsorption behavior is influenced by specific surface area of absorbent. However, the chloride adsorption capacity of MC is comparable to that of RHC although the fineness of MC is lower than RHC. In this study, it is assumed that C-S-H compounds are responsible for absorbing chloride ions, namely the physically bound chloride. Also C-S-H gel has the large surfaces. This implies that physically bound chloride content is not dependent on the fineness of cement, but the surface area, approximately the quantities of C-S-H produced. From Fig. 6, the same tendency as the physically bound chloride is confirmed for the contents of the chemically bound chloride; OPC has the highest capacity, whereas LHC has the lowest capacity, and MC and RHC have almost the same is comparable to to form Friedel's salt. This phenomenon reflects the C_3A contents in the cements (Table 2).

Moreover, it is found that the contents of physically bound chloride are much larger than those of the chemically bound chloride in the different cement types and at the different W/C, and that the physically bound chloride is the major part of the bound chloride. The content of the physically bound chloride, generally, ranges from 60% to 80% of the total amount of bound chloride (Fig. 7).

Isotherm of adsorption is presented as a function of concentration of free chlorides in solution. However, in this study, the chloride ions are not distributed uniformly. In other words, the chloride ions are not in equilibrium across the section, but locally in equilibrium. Thus we cannot determine exactly the equilibrium concentration of chloride ions in solution. From this reason, the authors intend to represent the isotherm of binding chlorides as a function of free chlorides in paste.

Fig. 8 shows the isotherm of chloride bound by AFm hydrate in cement pastes. The amount of the chemically bound chloride by AFm hydrate increases with increasing the AFm hydrate. The highest chloride binding capacity of AFm hydrate is 1.4 mol per 1 mol of AFm at a free chloride concentration of 26.8 mmol/l. This value is lower than the stoichiometric value of 2 mol chloride per 1 mol of AFm hydrate (Eq. 5).

$$C_3A.CaSO_4.H_{12} + 2NaCl \rightarrow C_3A.CaCl_2.10H_2O + 2Na^+ + SO_4^{2-} + 2H_2O \qquad (5)$$
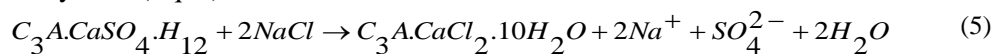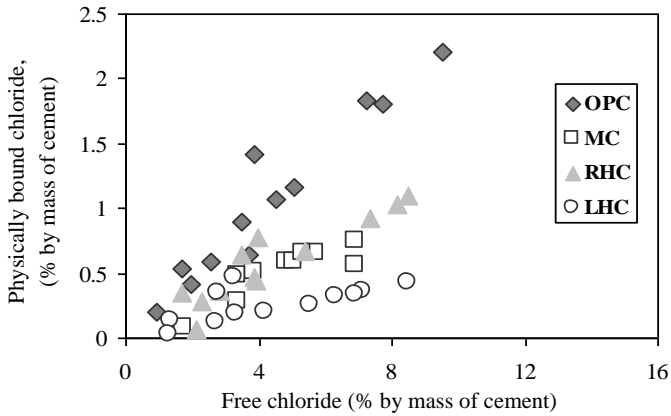
Fig. 5 Relationship between physically bound chloride and free chloride of various cement types
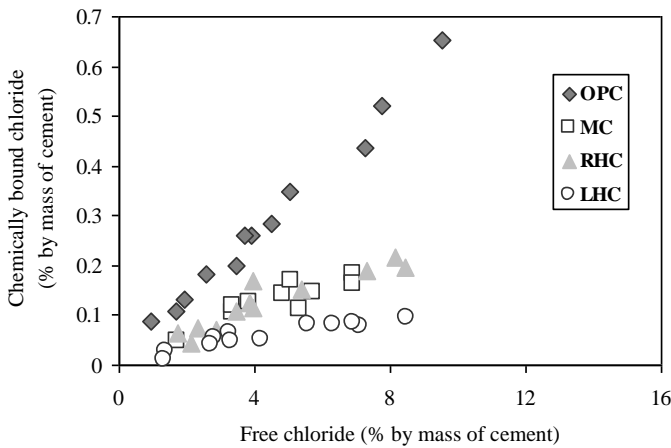

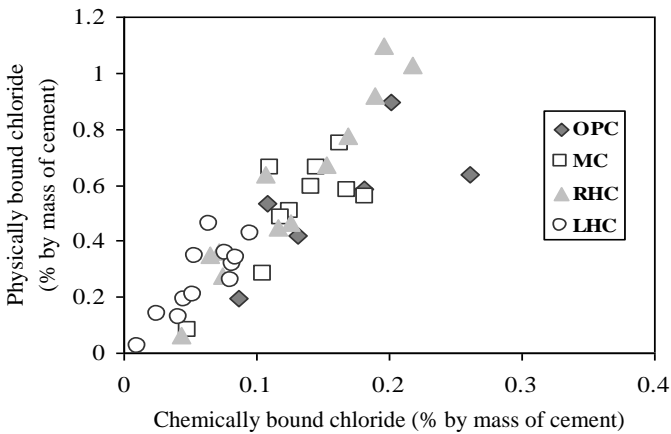Fig. 6 Relationship between chemically bound chloride and free chloride of various cement types

Fig. 7 Relationship between physically bound chloride and chemically bound chloride
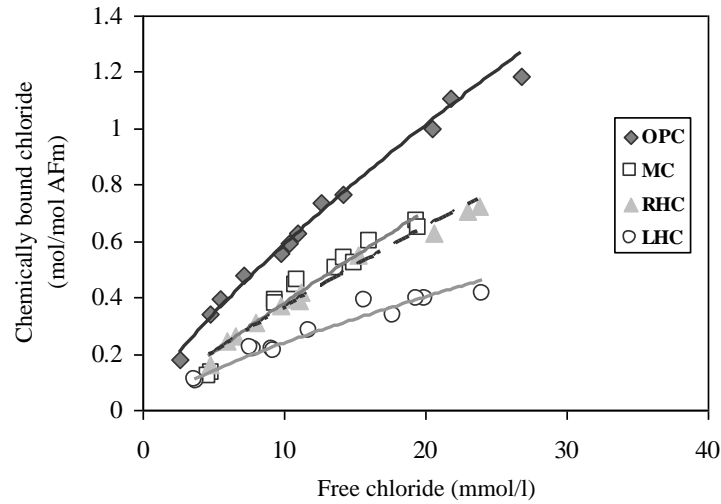
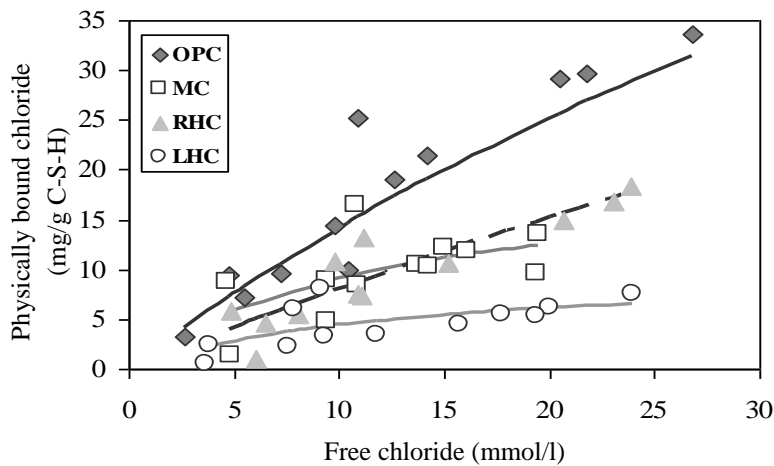Fig. 8 Chloride binding capacity of AFm hydrate of various cement types

Fig. 9 Chloride binding capacity of C-S-H hydrate of various cement types

Hirao *et al*. 2005 found that 1 mol of AFm bound 1.1 mol of chloride, whereas, Saeki *et al*. 2002 reported that this ratio was 5:1. According to the anion-exchange mechanism (Johannesson *et al*. 2007), this fact can be explained; other ions except for chloride ion such as SO_4^{2-} and CO_3^{2-} replaces into ion exchange sites on AFm, and prevent to form Friedel's salt. As shown in Fig. 8, the isotherm of chloride bound by AFm is Freundlich type isotherm as given by following equation.

$$C_a = \alpha C_l^{\beta} \tag{6}$$

where C_a:the amount of bound chlorides (mg/g), C_l:the free chloride concentration in solution

(mmol/l), α and β :constans.

The isotherms of chloride bound by unite mass of AFm are dependent on cement types. Experimental data fit the isotherm of chloride bound by AFm of various cement types as below:

$$\text{OPC:} \quad y = 0.0949x^{0.7888} \quad ; R^2 = 0.988 \tag{7}$$

$$\text{MC:} \quad y = 0.0473x^{0.901} \quad ; R^2 = 0.999 \tag{8}$$

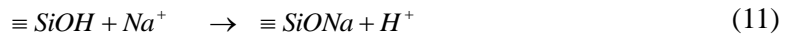$$\text{RHC:} \quad y = 0.0521x^{0.8408} \quad ; R^2 = 0.976 \tag{9}$$

$$\text{LHC:} \quad y = 0.0407x^{0.7623} \quad ; R^2 = 0.963 \tag{10}$$

where, x is the free chloride concentration (mmol/l) and y is the chemically bound chloride content (mol/mol AFm).

Fig. 9 shows the isotherm of chloride bound by C-S-H. It is clearly shown that the amount of chloride bound by C-S-H increases with increasing the free chloride concentration, and the isotherm of chloride bound by C-S-H can be fitted to the curve of a Langmuir isotherm type.

The highest chloride binding capacity of C-S-H hydrate is around 33.58 mg per 1 g of C-S-H phase, this is 1/3 of the chloride bound by AFm hydrate (Fig. 9), however the mass content of C-S-H hydrate in the cement paste is always much higher than that of the AFm phase, in some cases reaching nearly 66% weight of the cement paste. Consequently, the contribution of C-S-H hydrate to the chloride binding capacity of cement pastes is very significant.

Moreover, as shown in Fig. 9, the isotherms of chloride bound by C-S-H varied by cement types. Sodium, potassium, chloride and sulfate ions can be adsorbed on the surface of C-S-H as shown in Eqs. (11)-(14). Thus, the difference in isotherm with cement types can explain the same reason as the chemical bonding chlorides; other ions except for chloride ion adsorbed on the adsorption sites on C-S-H, and prevent adsorption of chlorides.

$$\equiv SiOH + Na^+ \quad \rightarrow \quad \equiv SiONa + H^+ \tag{11}$$

$$\equiv SiOH + K^+ \quad \rightarrow \quad \equiv SiOK + H^+ \tag{12}$$

$$\equiv SiOH + Ca^{2+} + Cl^- \rightarrow \quad \equiv SiOCaCl + H^+ \tag{13}$$

$$\equiv SiOH + Ca^{2+} + SO_4^{2-} \rightarrow \quad \equiv SiOCaSO_4^- + H^+ \tag{14}$$

The isotherms of chloride bound by C-S-H phase of the various cement types are expressed by Langmiur type adsorption isotherm curves as follows:

$$\text{OPC:} \quad y = 116.405 \frac{0.0138x}{1 + 0.0138x} \tag{15}$$

$$\text{MC:} \quad y = 20.355 \frac{0.0805x}{1 + 0.0805x} \tag{16}$$

$$\text{RHC:} \quad y = 133.156 \frac{0.0064x}{1 + 0.0064x} \tag{17}$$

$$\text{LHC:} \quad y = 10.0313 \frac{0.0777x}{1+0.0777x} \tag{18}$$

where, x is the free chloride concentration (mmol/l) and y is the physically bound chloride content (mg/g C-S-H).

3.3 Experimentally established equations to estimate the bound chloride of various cement pastes

As mentioned above, the C-S-H phase is responsible for the absorption of physically bound chloride, while the chemically bound chloride is formed due to the reaction of AFm hydrate with chloride ions present in the pore solution. Hence, the proposed equations used to estimate the bound chloride content of various cement pastes must be described basing on the contents of AFm and C-S-H hydrates. The experimentally established equations are as follows:

$$\text{OPC:} \quad y = 116.405 \frac{0.0138x}{1+0.0138x} \frac{n}{100} + 0.0949x^{0.7888} \cdot \frac{1000}{623} \cdot \frac{35.5m}{100} \tag{19}$$

$$\text{MC:} \quad y = 20.355 \frac{0.0805x}{1+0.0805x} \frac{n}{100} + 0.0473x^{0.901} \cdot \frac{1000}{623} \cdot \frac{35.5m}{100} \tag{20}$$

$$\text{RHC:} \quad y = 133.156 \frac{0.0064x}{1+0.0064x} \frac{n}{100} + 0.0521x^{0.8408} \cdot \frac{1000}{623} \cdot \frac{35.5m}{100} \tag{21}$$

$$\text{LHC:} \quad y = 10.0313 \frac{0.0777x}{1+0.0777x} \frac{n}{100} + 0.0407x^{0.7623} \cdot \frac{1000}{623} \cdot \frac{35.5m}{100} \tag{22}$$

where, x is the free chloride concentration (mmol/l), y is the amount of chloride ions bound by hydrates (mg/g sample), n is the amount of C-S-H gel in cement paste (mass%), and m is the amount of AFm hydrate (mass%).

As shown in Eqs. (19)-(22), the content of chloride ions bound by hydrates includes functions of parameters as AFm content, C-S-H content, and free chloride concentration. These experimental equations can be applied to all commonly used cement types with the assumptions that AFm is formed by the hydration of C_3A, that all AFm reacts with chloride ions to form Friedel's salt, and that AFm does not change to AFt at low chloride concentrations. This assumption is consistent with other reported results (Hirao *et al*. 2005, Nielsen *et al*. 2005).

Several methods have been proposed to determine hydrated cement phases (Termkhajornkit *et al*. 2005), and applying the experimentally determined equations described above together with the methods of determining hydrated cement phases, makes it possible to estimate the bound chloride content of various cement pastes from the contents of (C_3S+C_2S) and C_3A in the cement, and from the free chloride concentration.

4. Conclusions

This study investigates chloride binding isotherms for various types of cement. The total chloride content and the free chloride content were determined by experiments following

ASTM C 1152 and ASTM C 1218, respectively. The XRD Rietveld analysis was used to determine the contents of C-S-H, AFm hydrates and Friedel's salt. The results suggest the following conclusions:

• Of the four cement types, OPC has the highest capacity to bind chloride ions, whereas LHC has the lowest chloride ion binding capacity. The chloride binding capacities of MC and RHC are comparable.

• The AFm is responsible for binding chemically bound chloride by the formation of Friedel's salt, the isotherm of chloride bound by AFm can be fitted to the Freundlich isotherm, and 1 mol of AFm binds 1.4 mol chloride at a free chloride concentration of 26.8 mmol/l. The C-S-H binds the physically bound chloride, the isotherm of chloride bound by C-S-H can be fitted to a Langmuir isotherm and at a free chloride concentration of 26.8 mmol/l, the amount of physically bound chloride is 33.58 mg/g C-S-H. At a given bound chloride content, the amount of physically bound chloride is always much higher than that of the chemically bound chloride.

• Experimentally established equations are proposed to estimate the amounts of bound chlorides in different cement pastes made from various cement types. The parameters included in these equations are the free chloride concentration, the contents of AFm, and C-S-H hydrates.

Acknowledgments

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