Chloride Binding of Cement Estimated by Binding Isotherms of Hydrates

Hiroshi Hirao¹, Kazuo Yamada², Haruka Takahashi³ and Hassan Zibara⁴

Abstract

Chloride binding behaviors of cement, which is important for estimating the chloride penetration into concrete, are investigated. Firstly chloride binding isotherms of major cement hydrates are examined and then a chloride binding isotherm of cements is estimated from the binding isotherms of these hydrates. The results show that the monosulfate hydrate and C-S-H phases have significant chloride binding capacities, whereas ettringite and portlandite have no capacity to bind chlorides. However, there is a possibility that ettringite in cement paste dissolves at high chloride concentration to produce Friedel’s salt. The chloride binding by monosulfate hydrate is attributed to the formation of Friedel’s salt and the binding isotherm shows a good fit to a Freundlich-type adsorption. The chloride-binding isotherm of C-S-H shows a good fit to a Langmuir-type adsorption. The binding capacity of C-S-H is saturated at about 0.6 mmol/g at high chloride concentration over than 2 M. Based on the chloride binding isotherm of monosulfate hydrate and C-S-H, the chloride binding isotherms of cements are shown to be realistically predicted.

1. Introduction

Chloride-induced corrosion is a major problem for the durability of reinforced concrete structures. Chloride ions penetrate into a concrete cover through the pore solution in the concrete, and once the chloride concentration at the surface of rebars exceeds a certain value, chloride ions destroy the passive film on rebars and results in the initiation of steel corrosion. In order to estimate the life of reinforced concrete from the aspect of chloride corrosion, various models for chloride penetration have been proposed (Japan Society of Civil Engineers. 2000; Zibara et al. 2002a).

Chloride ions are found in concrete in two forms; one as free chloride in the pore solution, and the other as bound chloride in some form to cement hydrates. This means when chloride ions penetrate from external environments into concrete, they react with cement hydrates, and some are bound by the hydrates, while the rest remain free in the pore solution of concrete. It is only the free chloride ions that can penetrate deeper inside the concrete cover through the pore solution to reach the steel surface and initiate corrosion. Hence, the binding of chloride retards the penetration process, and consequently extends the initiation time of corrosion. Therefore, it is important, when modeling the penetration process, to take into account chloride binding by cement hydrates in addition to the diffusion and the movement of water.

The hydrates composing a hardened cement paste are diverse depending on the type of cement, age, mix proportions, and the degree of hydration. However, the major phases are, C-S-H (CaO-SiO₂-nH₂O), portlandite (Ca(OH)₂), ettringite (AFt: C₃A·3CaSO₄·32H₂O), and monosulfate hydrate (AFm: C₃A·CaSO₄·12H₂O). Regarding the mechanism of chloride binding, two forms are proposed: one is the chemical binding through the formation of Friedel’s salt (C₃A·CaCl₂·10H₂O), and the other is the physical binding by C-S-H typically. Friedel’s salt is a hydrate having a similar structure with AFm but the sulfate ion is replaced by two chloride ions. On the other hand, C-S-H is thought to show a binding behavior for many kinds of ions as well as chloride ion because of its very large surface area. Although the mechanisms of chloride ion binding by these hydrates have been investigated (Zibara. 2001; Zibara et al. 2002b), the contribution ratio of each phase is not clear yet.

In this study, chloride binding behavior of cement paste is tried to be estimated from the chloride binding isotherms of each cement hydrates. In order to clarify the contribution of each cement hydrate to the chloride binding of hydrated cement, the chloride-binding isotherms of major cement hydrates are investigated. Based on the results, an attempt is made to estimate the chloride-binding isotherm of OPC (Ordinary Portland Cement) and Ecocement.

2. Experiments

2.1 Materials

AFm was synthesized as follows: C₃A, gypsum and water were mixed at molar ratios of 1:1.5 respectively, then cured at 20°C for 4 days. C-S-H was prepared by mixing synthesized C₃S with water at a water to solid ratio of 10 at 20°C, and cured for 56 days under sealed condition. AFt

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was synthesized from reagent grade portlandite, Al₂(SO₄)₃, and water by mixing in a vibrating mill for 1 minute. Each hydrate was immersed in an excessive amount of acetone before being dried under 11%RH. As for portlandite, a reagent grade calcium hydroxide was used for the test. These hydrates were used for sorption test as synthesized and received condition without special treatment.

2.2 Sorption tests and analysis

The method employed for chloride sorption test is similar to the technique given by Tang et al. (1993). Chloride sorption tests by hydrates were carried out under the mixing ratio of 10 cm³ of NaCl solution and 1 g of hydrates. The mixture was kept at 20°C for 2 days, then the mixture was separated into solid and liquid phases by suction filtering, the former was used for the analysis of hydrates and the latter for the analysis of chloride ions. The saturation of sorption within two days was confirmed by separated tests. The solid phase was immersed into an excessive amount of acetone and dried under 11%RH before the analysis of hydrates by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and scanning electron microscope (SEM). The chloride concentration in the liquid phase was determined by ion chromatography.

3. Results and discussions

3.1 AFm

Friedel’s salt is an important product of chloride binding because it contains chlorine in its structure. When cement reacts with water in the presence of chloride ions, the C₃A and C₂AF phases react with chloride as shown in Eq. 1 to form Friedel’s salts. When chloride ions penetrate into concrete from external environments, many calcium aluminate hydrates, including AFm, bind chloride ions (Zibara. 2001; Zibara et al. 2002b). The AFm phase binds chloride ions as shown in Eq. 2.

\[
\begin{align*}
\text{C}_3\text{A} + 2\text{NaCl} + \text{Ca(OH)}_2 + 10\text{H}_2\text{O} & \rightarrow \text{C}_3\text{A}·\text{CaCl}_2·10\text{H}_2\text{O} + 2\text{Na}^+ + 2(\text{OH})^- \\
\text{C}_3\text{A}·\text{CaSO}_4·12\text{H}_2\text{O} + 2\text{NaCl} & \rightarrow \text{C}_3\text{A}·\text{CaCl}_2·10\text{H}_2\text{O} + 2\text{Na}^+ + \text{SO}_4^{2-} + 2\text{H}_2\text{O}
\end{align*}
\]

(1) Chloride binding isotherm of AFm

In order to calculate the binding capacity, the difference between the chloride concentration before and after sorption tests assumed to be the bound chloride by AFm. The amount of bound chloride was expressed as mol of chloride by 1 mol of AFm. The result is shown in Fig. 1. With the increase of chloride concentration of solution phase, the amount of bound chloride by AFm increases. The relationship shows a Freundlich isotherm. The amount of bound chloride at the initial chloride concentration of 5 M, is only 1.1 mol per 1 mol of AFm. This value is significantly lower than 2 mole of the stoichiometric value.

(2) Results of XRD test

When AFm is exposed to a chloride solution, Kuzel’s salt is reported to be formed at lower chloride concentrations, and Friedel’s salt is formed at higher chloride concentrations (Glasser et al. 1999; Zibara. 2001; Zibara et al. 2002b). XRD pattern from 8 to 12° (2θ, CuKα) after the immersion into chloride solution is shown in Fig. 2. The diffraction peak of AFm decreases with the increase of chloride concentration and it disappears over than 1 M of chloride concentration. On the other hand, a diffraction peak between 9.9° of AFm and 11.2° of Friedel’s salt is shifted to closer to Friedel’s salt with the increase of chloride concentration. Over the condition of 1 M of chloride concentration where the diffraction peak of AFm disappears, a peak expected to be Friedel’s salt is detected. This result coincides with the result of the analysis of
This indicates that AFm is transformed to Friedel's salt by ion exchange and the partial formation of solid solution at higher chloride concentrations.

Because the diffraction peak between AFm and Friedel's salt is ambiguous, the formation of Kuzel's salt, which has a peak at 10.4°, is difficult to identify in this experiment. The diffraction peak of AFt increases gradually until the chloride concentration of 1 M where the diffraction peak of AFm disappears. The increase in the quantity of AFt is attributed to the increase of SO$_4^{2-}$ ion concentration as a result of ion exchange with chloride ion as shown in Eq. 2. The formation of AFt from AFm described in Eq. 3 may be assumed to occur by dissolution and precipitation (Taylor, 1997). In the range of the chloride concentration of 1 to 5 M, with increase of chloride concentration the peak of Friedel's salt increase slightly, but the peak of AFt decreases suddenly. Nonetheless, the more increase of SO$_4^{2-}$, the diffraction peak of AFt decreases. This suggests the possibility of dissolution of AFt under a high concentration of chloride.

$$C_3A\cdot CaSO_4 \cdot 12H_2O + 2Ca^{2+} + 2SO_4^{2-} + 20H_2O \rightarrow C_3A\cdot 3CaSO_4 \cdot 32H_2O$$ (3)

(3) Shape of hydrates

Secondary electron images of AFm are shown in Fig. 3. The morphology of AFm before immersion into chloride solution is typical plate form. The result of XRD indicates that at 5 M of initial chloride concentration the major hydrates is only Friedel's salt, and no AFm is present. However, the morphology of crystals is the same as those of AFm. This suggests that the transformation from AFm to Friedel’s salt occurred by ion exchange of SO$_4^{2-}$ ions with Cl$^-$ ions, keeping the fundamental structure the same.

(4) Chloride binding isotherm calibrated by the amount of hydrates

The result described above indicates that the formation of Friedel’s salt is caused by ion exchange between SO$_4^{2-}$ and Cl$^-$ and this ion exchange is judged to be the major mechanism of chloride binding. However, minor phase such as AFt forms simultaneously in some degree. Therefore, the chloride binding isotherm is different from the system of pure AFm-Friedel’s salts. In this study, the amount of Friedel’s salt is quantified by DSC and is used to calibrate the binding isotherm.

The calibrated binding isotherm is shown in Fig. 4. The bound chloride increases in all range of chloride concentration. By the calibration, the amount of bound chloride at a high chloride concentration becomes close to 2.0 mol/mol-AFm, the theoretical value. From this result, chloride binding by AFm phase is judged to be attributed in the stoichiometric formation of Friedel’s salt and the adsorption on the surface of AFm is limited.

It is necessary to be aware of one point: because the solid solution between AFm and Friedel’s salt is thought to contain significant amount of sulfate ion in the chloride ion concentration lower than 1 M from the results of XRD, it is not easy to quantify the amount of the solid solution of AFm-Friedel’s salt only from the range of this study. Because of this reason, there is an uncertainty in the quantification of Friedel’s salt.
3.2 C-S-H

The mechanism of chloride binding by C-S-H is reported to be physical sorption that is different from the ion exchange of AFm (Theissing et al. 1980). Several different results of chloride binding capacity of C-S-H have been reported. Lambert et al. (1985) reported no chloride binding when alite was immersed into NaCl solution for 200 days. On the other hand, other researches found significant binding capacity of C-S-H pastes (Wowra et al. 1997; Zibara 2001; Zibara et al. 2002b). Nakamura et al. (1999) reported that 1g of C-S-H bound 172 mg of chloride when synthesized C-S-H was immersed into 0.9% chloride solution at the water to solid ratio of 1000. Possible reasons for these differences are the variety of chemical composition and surface area of C-S-H as well as the differences in the kind of chloride or experimental conditions. In this study, C-S-H produced by the hydration of synthesized alite, which is expected to have similar characteristics to that in real concrete was used to investigate its binding behavior of chloride.

(1) Chloride binding isotherm by C-S-H

The chloride binding capacity of C-S-H was calculated in the same way as that of AFm (section 3.1(1)). The chloride binding isotherm is shown in Fig. 5. The amount of bound chloride increases with the increase of chloride concentration. The binding isotherm is non linear and shows a good fit to the regression curve of Langmuir-type adsorption isotherm. The chloride binding capacity is saturated at 0.4 mmol/g, which is 1/5 of that of the AFm phase. However, because the mass ratio of C-S-H in Portland cement concrete is much higher than AFm, for chloride binding capacity of concrete the contribution of C-S-H is significant.

(2) Calibration of chloride binding isotherm

Secondary electron images of C-S-H are shown in Fig. 6. The morphology of hydrates is almost identical before and after sorption test. Because hydrated alite was used in this study, the formation of Ca(OH)$_2$ was detected by XRD analysis. Therefore, the amount of Ca(OH)$_2$, which has no chloride binding capacity as will be discussed in section 3.4, was quantified by DSC and the chloride binding isotherm of C-S-H was calibrated to that of pure C-S-H. The result is shown in Fig. 7. The shape of isotherm is maintained same. The maximum binding capacity of C-S-H is increased to 0.60 mmol/g.
3.3 AFt
The chloride-binding isotherm of AFt is shown in Fig. 8. AFt shows no binding capacity even at high chloride concentration. Secondary electron images of AFt before and after sorption test are shown in Fig. 9. The morphology of hydrates is the same before and after immersion. No other phase than AFt was detected by XRD.

3.4 Ca(OH)₂
The chloride binding isotherm of Ca(OH)₂ is shown in Fig. 10. The results indicate that Ca(OH)₂ does not exhibit any chloride binding capacity. Judging from secondary elec-
tron images before and after sorption test as shown in Fig. 11, the morphology of Ca(OH)$_2$ remains unchanged. No other phase was detected by XRD.

3.5 Estimation of chloride binding by cement paste

As shown above, AFm and C-S-H show significant amount of chloride binding. However, AFt and Ca(OH)$_2$ show no significant capacity to bind chloride. Assuming that a cement paste is mainly composed of these four phases, it is then possible to estimate the chloride binding capacity of cement paste from the content of AFm and C-S-H by Eq. 4.

$$y = 0.616 \times \frac{2.65x}{1 + 2.65x} \times \frac{a}{100} + 0.859 \times \frac{1000}{623} \times \frac{b}{100}$$

where, $x$ is the chloride concentration in solution phase (mol/l), $y$ is the amount of chloride bound by hydrates (mmol/g), $a$ is the content of C-S-H (mass%), and $b$ is the content of AFm (mass%).

As an example of experimental data, the chloride binding isotherms by the authors (Hirao et al. 2004) that are OPC and Ecocement paste having water to cement ratio of 0.5 at the age of 4 months are plotted in Fig. 12. The mineral composition of cement used is shown in Table 1. The relationship between the chloride concentration and the amount of bound chloride shows a Freundlich isotherm although some researchers reported it shows a linear binding (Page et al. 1991). As an example of estimation, based on a published method of calculation of hydrated cement phases (Japan Concrete Institute. 1996), the phase composition of cement paste is calculated. Amount of AFt and Ca(OH)$_2$ are determined by XRD and DSC, respectively. The phase composition of cement paste is calculated by using these experimental results and the assumptions listed below.

1) All of gypsum reacts with C$_3$A and C$_4$AF. After gypsum consumed, C$_3$A and C$_4$AF react with Ca(OH)$_2$ and then produce C$_4$AH$_{13}$.

2) Amount of C-S-H is determined by reaction ratio of C$_3$S and C$_2$S, and amount of Ca(OH)$_2$. The reaction ratios of cement minerals used in this calculation are shown in Table 2 (Japan Concrete Institute. 1996). The reaction ratios in Table 2 were determined by XRD with internal standard.

As shown in Table 3, the phase compositions of cements are calculated, and then chloride binding isotherms of cements are estimated by Eq. 4 and plotted in Fig. 12. The measured bound chloride of OPC and Ecocement paste are a little bit higher than the chloride binding isotherm estimated by Eq. 4. As described above, at a high chloride concentration, there is a possibility that AFt in cement paste dissolves and then converts to the product of Friedel's salt. Warren et al. (1994) reported that AFt converts to AFm through the substitution of OH$^-$ for SO$_4^{2-}$ in AFt especially at pH value greater than 13. In the high pH solution with much amount of chloride ion, AFt is attributed to convert to Friedel's salt instead of AFm. The

<table>
<thead>
<tr>
<th>Table 1 Mineral composition of cement used (mass%).</th>
<th>Ecocement</th>
<th>OPC</th>
</tr>
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<tbody>
<tr>
<td>C$_3$S</td>
<td>57</td>
<td>65</td>
</tr>
<tr>
<td>C$_2$S</td>
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<tr>
<td>C$_4$AF</td>
<td>12</td>
<td>9</td>
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<table>
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<tr>
<th>Table 2 Reaction ratios of cement minerals (%).</th>
<th>C$_3$S</th>
<th>C$_2$S</th>
<th>C$_3$A</th>
<th>C$_4$AF</th>
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</thead>
<tbody>
<tr>
<td>Ecocement</td>
<td>73.4</td>
<td>21.0</td>
<td>83.0</td>
<td>35.7</td>
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<tr>
<td>OPC</td>
<td>65.2</td>
<td>16.0</td>
<td>19.0</td>
<td>22.0</td>
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<table>
<thead>
<tr>
<th>Table 3 Phase composition of cement paste (mass%).</th>
<th>Ecocement</th>
<th>OPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$S</td>
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<td>3.4</td>
</tr>
<tr>
<td>C$_2$S</td>
<td>3.7</td>
<td>8.3</td>
</tr>
<tr>
<td>C$_3$A</td>
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<td>C$_4$AF</td>
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<td>5.2</td>
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<tr>
<td>CaSO$_4$</td>
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<td>0.0</td>
</tr>
<tr>
<td>AFt</td>
<td>5.4</td>
<td>4.0</td>
</tr>
<tr>
<td>AFm</td>
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<tr>
<td>CH</td>
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<td>8.4</td>
</tr>
<tr>
<td>C$<em>4$AH$</em>{13}$</td>
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</tr>
<tr>
<td>C-S-H</td>
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<td>43.3</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>15.4</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Fig. 12 Chloride binging isotherms, estimation and experiments.
chloride binding isotherms are recalculated by using assumption that AFt can produce Friedel’s salt in a way similar to AFm. It is assumed that 1mol of AFt converts to 1 mol of AFm. In the recalculation of the chloride binding isotherms estimated by using Eq. 4, the content of AFm in the cement paste includes AFm converted from AFt. The results are also plotted in Fig. 12.

The recalculated chloride binding isotherms show a good coincidence with the data of cement pastes. This indicates that at least for OPC and Ecocement, if it is possible to estimate the content of C-S-H and AFm, the chloride binding isotherm can be estimated from the chloride binding isotherm of individual hydrates, and AFt in cement paste is possible to contribute to chloride binding especially at high chloride concentration, as shown in this study.

The phases that bind chloride are hydrates but not unhydrated cement. This means that the degree of hydration significantly affects the chloride binding capacity and the chloride binding capacity depends on water to cement ratio and age because the degree of hydration is affected by these factors. Therefore, even in a lower water to cement ratio or at a relatively early age, if the degree of hydration is estimated, the chloride binding isotherm of cement paste can be estimated by the method described in this study.

4. Conclusions

In order to supply data of chloride binding isotherm for the estimation of chloride penetration into concrete by numerical models, chloride binding isotherms of individual hydrates composing cement paste are investigated.

1) Chloride binding by AFm is attributed to the formation of Friedel’s salt. Chloride binding isotherm is fitted to Freundlich type successfully. The amount of bound chloride at 5 M of chloride concentration is equal to the theoretical value of 2 mol/mol-AFm.

2) Chloride binding by C-S-H is fitted to Langmuir type successfully. The saturated amount of bound chloride is 0.6 mmol/g.

3) AFt and Ca(OH)2 show no chloride binding capacity. However, AFt in cement paste is possible to dissolve at a high chloride concentration and then produce Friedel’s salt.

4) From the chloride binding isotherms of AFm and C-S-H, the chloride binding isotherm of OPC and Ecocement pastes can be estimated with the information of the phase compositions of pastes.

References


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