

Prediction of chloride binding isotherms for blended cements

Hailong Ye^{*1,3}, Xianyu Jin^{1a}, Wei Chen¹, Chuanqing Fu^{1,2} and Nanguo Jin^{1b}

¹College of Civil Engineering and Architecture, Zhejiang University, Hangzhou 310058, P.R. China

²College of Civil Engineering and Architecture, Zhejiang University of Technology, Hangzhou 310034, P.R. China

³Department of Civil and Environmental Engineering, The Pennsylvania State University, 3127 Research Drive, State College, PA, 16801, United States

(Received January 15, 2016, Revised February 14, 2016, Accepted February 15, 2016)

Abstract. A predictive model for chloride binding isotherms of blended cements with various supplementary cementitious materials (SCMs) was established in this work. Totally 560 data points regarding the chloride binding isotherms of 106 various cements were collected from literature. The total amount of bound chloride for each mixture was expressed a combinational function of the predicted phase assemblage and binding isotherms of various hydrated phases. New quantitative expressions regarding the chloride binding isotherms of calcium-silicate-hydrate (C-S-H), AFm, and hydroalcalite phases were provided. New insights about the roles of SCMs on binding capabilities of ordinary portland cements (OPC) were discussed. The proposed model was verified using separate data from different sources and was shown to be reasonably accurate.

Keywords: cement; corrosion; degradation; computer-aided design & integration; reinforced concrete (RC)

1. Introduction

Chloride-induced corrosion has been a major cause for the premature structural deterioration of reinforced concrete structures built in a marine or deicing salts environment (Neville 1995, Vu and Stewart 2000). The initiation of corrosion is accompanied by the disappearance of initially formed passive film around rebars, when the chloride concentration at the surface of rebar reaches a critical threshold (Angst *et al.* 2009). In order to accurately estimate the initiation time of rebar corrosion in concrete structures, extensive research regarding the prediction of the chloride ingress into concrete has been conducted over decades (Amey *et al.* 1998, Boulfiza *et al.* 2003, Fu *et al.* 2015, Mien *et al.* 2009, Ye *et al.* 2015, Ye *et al.* 2012).

The chloride in concrete can either in the pore solution as free ions, or physically/chemically bound to hydration products of cementitious binders. The correlations between free and bound

* Corresponding author. E-mail: yehailong1@gmail.com

^aPh.D., Professor, E-mail: xianyu@zju.edu.cn

^bPh.D., Professor, E-mail: jinnng@zju.edu.cn

chloride ions over a range of chloride concentrations at a given temperature are known as the chloride binding isotherms. A reliable estimation of chloride binding isotherms of cementitious materials is crucial to accurately predict the service life of reinforced concrete structures (Martin-Pérez *et al.* 2000). Many researchers have attempted to propose various predictive models to estimate the chloride binding capabilities of cementitious materials. Roughly, these models can be categorized into two types: estimated by (i) chemical compositions of raw materials, and by (ii) binding isotherms of hydrated phases (Florea and Brouwers 2012, Hirao *et al.* 2005, Mien *et al.* 2014). For example, Zibara (Zibara 2001) proposed an approach to estimate the chloride binding isotherms of hardened ordinary portland cement (OPC) paste based on the mass percentages of clinker minerals and SO_3 . This empirical approach bases on fitting the chemical composition of raw materials to the experimental data of chloride binding capacities, which does not have any physical or chemical basis. The external chloride ions (as opposed to the internally-added chloride in concrete mixtures) are primarily bound by the hydration products of cementitious binders during the penetration process in most in-service reinforced concrete structures. As a consequence, predicting the chloride binding isotherms of cementitious materials basing on the binding capabilities of hydrates has shown great promises (Florea and Brouwers 2012, Hirao *et al.* 2005). Hirao *et al.* (Hirao *et al.* 2005) measured the chloride binding isotherms of synthetic calcium-silicate-hydrate (C-S-H), monosulfate, portlandite, and ettringite. They further proposed an expression to predict the chloride binding isotherms of OPC based on the mass fractions and binding capacities of C-S-H and AFm phases, since portlandite and ettringite have little binding capabilities (Hirao *et al.* 2005). Florea *et al.* proposed two models in which one merely considers the binding capabilities of C-S-H and AFm phases, while another one also considers the physical adsorption of chloride by portlandite and Friedel's salts. However, it was found that the chloride bound by portlandite and Friedel's salts accounts for only about 2-5% of the total bound chloride by OPC pastes (Florea and Brouwers 2012).

On the other hands, the prediction of chloride binding isotherms of cements blended with various supplementary cementitious materials (SCMs) was relatively scarcely reported and more challenging. Experimentally, it was reported that the incorporation of SCMs can dramatically modify the chloride binding capability of OPC depending on the chemical composition and SCMs replacement ratio (Arya *et al.* 1990, Baroghel-Bouny *et al.* 2012, Delagrave *et al.* 1997, Ipavec *et al.* 2013, Thomas *et al.* 2012, Zibara 2001). Typically, ground granulated blast-furnace slag, fly ash, and metakaolin enhance the chloride binding capability of cement, while silica fume reduces it (Delagrave *et al.* 1997). However, the modifying mechanisms on chloride binding capability by various SCMs are still controversial. For instance, the enhanced binding capabilities of slag-blended cements can be attributed to the high alumina content of slag (Luo *et al.* 2003), or to the $[\text{OH}]/[\text{Cl}]$ ratio (Arya and Xu 1995), or to the extensive hydrotalcite formation (Kayali *et al.* 2012), or to the denser pore structure (Loser *et al.* 2010).

The main objective of this study is to propose a new predictive model to estimate the chloride binding isotherms of blended cements containing various SCMs. It attempts to quantify the binding isotherms of the main hydrated phases in blended cements, including calcium-silicate-hydrates, AFm (hydroxy-AFm and monosulfoaluminate solid solution), and hydrotalcite phases, through a further analysis of published data in literature. Based on the proposed model, the binding isotherms of a given cementitious system can be estimated based on the phase assemblage and suggested binding isotherms of hydrates. Fig. 1 shows the flowchart describing the basic procedure for establishing the predictive model in this study. In addition, the role of SCMs on the binding capabilities of OPC was discussed, towards to a better understanding of the chloride binding

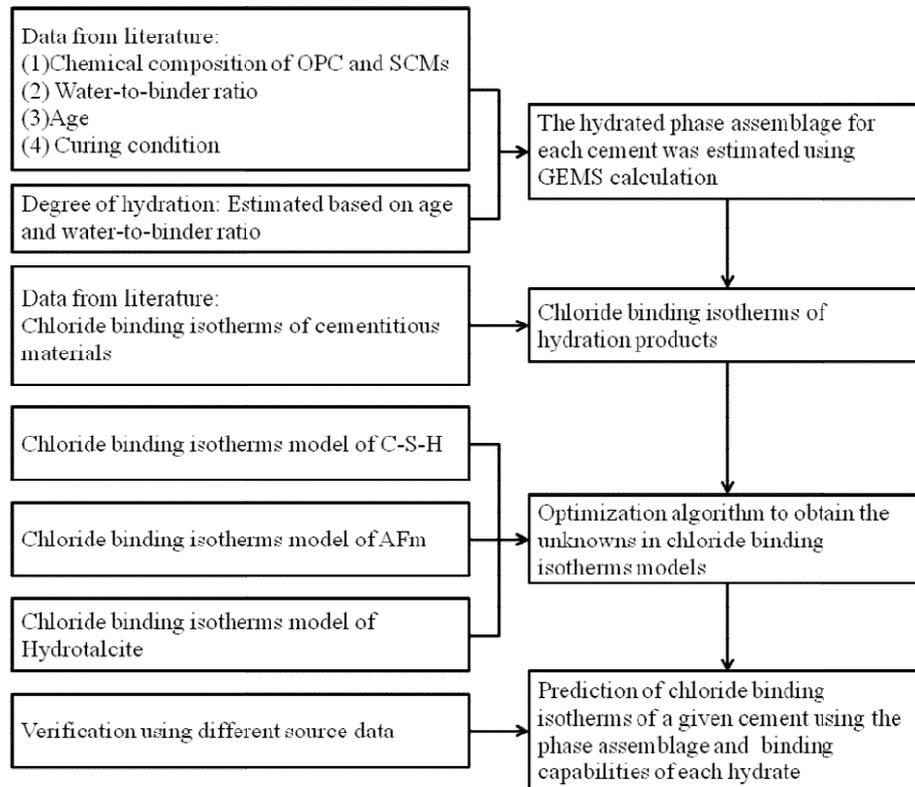


Fig. 1 Flowchart for establishing the predictive model for chloride binding isotherms of blended cements

mechanisms of blended cements.

2. Chloride binding isotherms of hydrated phases

2.1 Data selection from literature

The published data regarding the chloride binding isotherms of various cementitious materials were selectively collected. In literature, the ways of introducing chloride into cementitious systems can through either pre-mixing with cement (i.e. internal chlorides) or intruding from external sources (i.e. external chlorides). The chloride binding isotherms for a certain type of cementitious material can be different due to the way of adding chlorides (Arya *et al.* 1990). This study only collects the binding isotherms data for external chloride attack, since this circumstance is more concerned in realistic reinforced concrete structures. In addition, the chloride binding isotherms of cementitious materials depend on the type of cations (e.g. Na^+ , Ca^{2+} , or Mg^{2+}) associated with chlorides (De Weerd *et al.* 2014). Considering that sodium chloride (NaCl) is the dominant form of chlorides in the seawater and has been most widely investigated by previous researchers, this study focuses on the binding capability of cementitious materials due to sodium chloride intrusion. On the other hands, various researchers adopted different methods to determine the binding

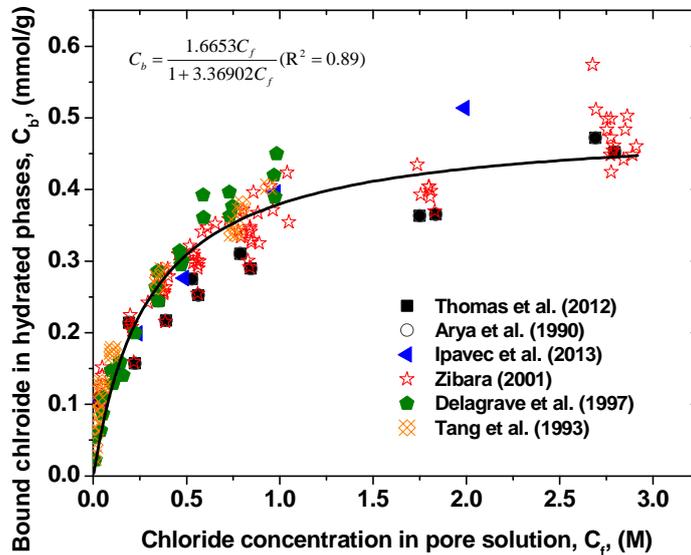
isotherms of cements, including equilibrium method (Tang and Nilsson 1993), pore solution expression (Sergi *et al.* 1992), and migration test method (Castellote *et al.* 1999). It is still unknown whether the results obtained by different testing methods are comparable. Therefore, this study adopts the data which was measured using the equilibrium method at room temperature that was originally proposed by Tang and Nilsson (Tang and Nilsson 1993). In a typical chloride binding isotherm measured by equilibrium method, the free chloride content is expressed as the chloride concentration (M), while the bound chloride is expressed as weight percentage of cementitious binders (i.e. mg/g). In this study, the binding isotherm data in which the chloride concentration in solution ranging from 0-3 M are included. In addition, the potential effect of alkalinity of pore solution on the binding isotherms is not distinguished.

After a careful selection of the published data in literature, totally 560 data points regarding the chloride binding isotherms of 106 different cements (including pure OPC and OPC with SCMs) from 7 different sources were implemented in this study, as listed in Appendix Table A1. In particular, the data from Thmoas *et al.* (Thomas *et al.* 2012), Arya *et al.* (Arya *et al.* 1990), Ipavec *et al.* (Ipavec *et al.* 2013), Zibara (Zibara 2001), Delagrave *et al.* (Delagrave *et al.* 1997), and Tang *et al.* (Tang and Nilsson 1993) were used to establish the predictive model as the 'training sets', while the data from Baroghel-Bouny *et al.* (Baroghel-Bouny *et al.* 2012) were used to verify the model.

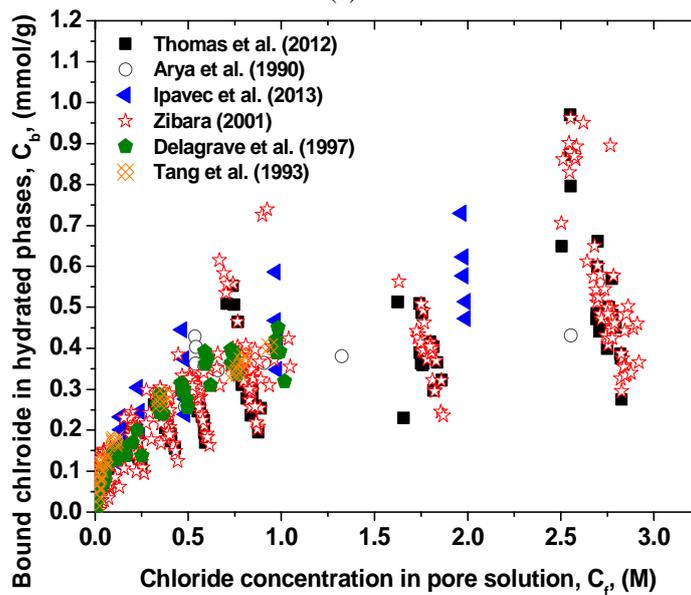
2.2 Data processing

Although there is tremendous available data in literature regarding the chloride binding isotherms of various cements, most of them are presented as the binding capability of sample (e.g. bound chloride (mg) / cementitious binder (g)) as a function of free chloride concentration in pore solution (M). In order to correlate the binding capabilities of various hydrates to the free chloride concentration in pore solution, the total amount of hydrated phases and the proportion of each hydrated phase for each mixture (as listed in Appendix) need to be estimated first. Regardless of the pure OPC or blended cements, the type and proportion of various hydrated phases are dependent on the chemical composition of OPC and SCMs, water-to-binder ratio, replacement ratio of OPC by SCMs, age, and curing condition. For all the cements listed in Appendix, the chemical composition of various OPC and SCMs, SCM replacement ratio, and water-to-binder ratio are available in the related references. The age is approximated as the time when the external chloride exposure was terminated and binding isotherms data were measured. In addition, most 'equilibrium method'-based method exposes the samples to a saturated condition during the chloride intrusion.

This study predicts the phase assemblage of each cement using GEMS thermodynamic calculation (will be elaborated later) based on the oxide compositions of OPC and SCMs, water-to-binder ratio, SCM replacement ratio. Prior to performing the GEMS calculation, the degree of hydration for each ingredient in the starting materials needs to be estimated unless it was reported in the literature (e.g. the data reported by Delagrave *et al.* (Delagrave *et al.* 1997)). For pure OPC, although the hydration kinetics among the various compounds (C_3S , C_2S , C_3A , C_4AF) would be different at early age, a global degree of hydration is reasonably accurate for all clinker minerals, when degree of hydration has progressed over 50% (Brouwers 2004). For blended cements, the degree of hydration of SCMs can be different from that of OPC, and can vary depending on the chemical composition and replacement ratio of SCMs. Considering that limited data available for separating the degree of hydration between OPC and SCMs, a global degree of hydration α was



(a)



(b)

Fig. 2 Chloride binding isotherm of hydrated phases in (a) OPC; (b) OPC blended with SCMs

approximated based on the water-to-binder ratio (w/b), and the age of samples t (in month) at the end of chloride exposure, using $\alpha = 0.716t^{0.0901} \exp[-0.103t^{0.0719}/(w/b)]$.

The thermodynamic calculation was performed by using the Gibbs Energy Minimization Software GEM-Selektor v.3, with the CEMDATA 14.01 and PSI-Nagra chemical thermodynamic databases (Kulik *et al.* 2003, B Lothenbach and Gruskovnjak 2007). Among all the oxide composition in OPC and SCMs, only the CaO, SiO₂, Al₂O₃, MgO, SO₃, Na₂O, and K₂O are

considered, due to the reason that they constitute more than 95% of the total mass of OPC and SCMs, and mainly account for the formation of hydrated phases. In addition, the activity coefficients of aqueous species were computed with the built-in expanded extended Debye-Hückel equation. All simulations were performed at a nitrogen atmosphere with the temperature and pressure conditions of 25 °C and 1 bar. It should be noted that under a CO₂-free condition, the carbonate-containing AFm phases (e.g. monocarboaluminate and hemicarboaluminate) are not expected to form. However, for realistic structural concrete exposed to the marine atmosphere or designed with intentional limestone addition (e.g. as a filler), the carbonation of hydrated phases is inevitable. The carbonation of hydrated phases (especially AFm) can release free chloride (i.e. lowering binding capability), which is attributed to the chloride ion in Friedel's salts replacement by carbonates (Lee *et al.* 2013, Ye *et al.* 2016). Nevertheless, due to the limited information regarding the carbonation of cements in relevant literature, as well as the specific testing procedure in 'equilibrium method' (i.e. the samples were immersed in solution), this model assumes that the formation of carbonate-containing phases is negligible.

After converting the binding isotherms of cementitious binders to the binding isotherms of hydrated phases based on the predicted phase assemblage, Fig. 2 shows the binding isotherms of hydrated phases in pure OPC and blended cements. It can be seen that for pure OPC, there is a strong correlation between bound chloride in hydrated phases and the free chloride concentration, which can be reasonably represented by a Langmuir-type isotherm model. This strong correlation indirectly implies that the estimation of hydrated phase assemblages using the thermodynamic calculation is reasonable. While for OPC blended with SCMs, this correlation is relatively poor. It indicates that the difference in binding capabilities of each hydrated phases would play an important role in blended cements since each mixture has a different phase assemblage. The following section will elaborate the method to predict the binding isotherms of blended cement based on the combination of binding isotherms of hydrated phases and predicted phase assemblage using thermodynamic calculation.

2.3 Chloride binding models for hydrated phases

In blended cement, although the proportion and type of various hydrated phases can vary, the solid phases that can considerably absorb chloride ions are AFm, C-S-H, and hydrotalcite phases. While other solid phases, including portlandite, AFt, hydrogarnet, Friedel's salts, and Kuzel salts, may be capable of binding chloride ions, but their contribution is eliminated due to the comparatively little binding capabilities.

The AFm family consists of a group of compounds, including monosulfate, hydroxy-AFm, monocarbonate and their solid solutions. Since the carbonated AFm phases (monocarbonate, hemicarbonate and any of their solid solutions) are not considered in the present study, the main AFm phase considered are monosulfate, hydroxy-AFm, and monosulfate-hydroxy-AFm solid solution. The chloride binding capabilities of pure monosulfate and hydroxy-AFm may be slightly different. However, pure AFm phase may not extensively exist but in a form of monosulfate-hydroxy-AFm solid solution in an un-carbonated circumstance. In addition, stratlingite can form in blended cements, especially with the increasing incorporation of alumina-rich SCMs. Although previous research has shown that stratlingite can transform into Friedel's salts at saline environments, but this process is at a much lower rate and much of the stratlingite persists at higher chloride concentrations (Zibara *et al.* 2008). Therefore, monosulfate-hydroxy-AFm solid solution as predicted by GEMS calculation is regarded as the only AFm phases in the proposed

model.

The chloride binding mechanisms of AFm phases are generally attributed to the ion-exchange mechanisms, in which chloride ion substitutes the sulfate or hydroxyl groups in the structure of different AFm-type compounds, forming chloride-containing phases such as Friedel's salt and Kuzel salt. Hirao *et al.* (Hirao *et al.*, 2005) quantified the binding isotherms of synthetic monosulfate phase using a Freundlich-type isotherm model

$$C_{b_AFm} = \alpha_{AFm} C_f^{\beta_{AFm}} \quad (1)$$

Where C_f is the free chloride concentration (M) in solution; α_{AFm} and β_{AFm} are constants for AFm chloride binding.

The C-S-H phase can physically bind chlorides ions through surface physical adsorption. The Ca/Si ratio of C-S-H in pure OPC is about 1.65, but can vary for blended cement (Richardson 2008). In addition, the alumina can incorporate into the structure of C-S-H for cement blended with alumina-rich SCMs (e.g. slag). All of these modifications in chemical composition and structure of C-S-H can potentially affect the binding capability of C-S-H. Unfortunately, the quantitative relationship between the binding isotherms of C-S-H and its chemical composition is still unknown. In addition, the modification of chemical composition in C-S-H in blended cements is not experimentally evidenced as the main reason accounting the altered binding behavior. Therefore, the C-S-H phase that is predicted in the GEMS calculation is included in this model, without distinguishing the altered chloride binding capabilities due to chemical variation. According to the research by Hirao *et al.* (Hirao *et al.* 2005), the Langmuir-type isotherm model, derived from physical chemistry, provides the best fitting for the binding isotherms of C-S-H

$$C_{b_C-S-H} = \frac{\alpha_{C-S-H} \cdot C_f}{1 + \beta_{C-S-H} \cdot C_f} \quad (2)$$

Where α_{C-S-H} and β_{C-S-H} are constants for C-S-H chloride binding.

Hydrotalcite (HT), a layered double hydroxide (LDH), was reported to be able to dramatically bind chloride ions and may be responsible for the enhanced binding capabilities of slag-blended cements (Kayali *et al.* 2012). The binding mechanism of hydrotalcite-type LDH is attributed to the ion-exchange process, in which the ions in the interlayer can be gradually substituted by the chloride ions (Yang *et al.* 2012). The quantification of binding capabilities of HT has not been exclusively addressed by previous researchers yet. The solid solution of various hydrotalcite-type phases may have different binding capabilities, and may vary depending on its chemical composition (e.g. Mg/Al ratio). In addition, the hydrotalcite-type LDH and chloride containing LDH may be able to physically absorb chloride ions, as Friedel's salt does. For simplification, this model assumes the predicted pure HT phase behave in a Langmuir-type isotherm

$$C_{b_HT} = \alpha_{HT} C_f^{\beta_{HT}} \quad (3)$$

Where α_{HT} and β_{HT} are constants for HT chloride binding. The difference between the Langmuir and Freundlich isotherms is their behavior at high concentrations. Choosing Langmuir-type isotherm model for HT phases is simply because of its analogous to AFm phases in term of binding mechanism.

Therefore, according to the proportion of each hydrated phases estimated using thermodynamic calculation, combined with the binding isotherms models for each phases as introduced above, solving the following equation can offer the solution to the best fitting parameters in binding isotherm models for each hydrated phase.

$$\min \sum_{i=1}^n \left(C_{b_mea,i} - \left(m_{C-S-H,i} \cdot \left(\frac{\alpha_{C-S-H} \cdot C_{f,i}}{1 + \beta_{C-S-H} \cdot C_{f,i}} \right) + \sum_{j=AFm,HT} m_{j,i} \cdot \alpha_j \cdot C_{f,i}^{\beta_j} \right) \right)^2 \quad (4)$$

S.t.

$$\alpha_{C-S-H}, \beta_{C-S-H}, \alpha_{AFm}, \beta_{AFm}, \alpha_{HT}, \beta_{HT} \geq 0 \quad (5)$$

Where n is the number of data points from literature; i is the index for the data points; $C_{b_mea,i}$ is the measured bound chloride in the hydrated phases (corrected by results from thermodynamic calculation) [mmol/g]; $C_{f,i}^{\beta_j}$ is the measured free chloride concentration in solution reported in literature [M]; $m_{j,i}$ is the GEMS predicted mass fraction of C-S-H, AFm phase, or hydrotalcite of a certain cement mixture corresponding to the data point i ; α_{C-S-H} , β_{C-S-H} , α_{AFm} , β_{AFm} , α_{HT} , and β_{HT} , are parameters to fit the chloride binding isotherms and have no physical meanings.

After operating the non-linear optimization algorithm using Excel Solver, the best fitting values for α_{C-S-H} , β_{C-S-H} , α_{AFm} , β_{AFm} , α_{HT} , and β_{HT} can be obtained. Therefore, the optimized chloride binding isotherms for C-S-H, AFm phases, and hydrotalcite phases can be re-written as

$$C_{b_C-S-H} = \frac{0.5722C_f}{1 + 3.2550C_f} \quad (6)$$

$$C_{b_AFm} = 1.1419C_f^{0.5007} \quad (7)$$

$$C_{b_HT} = 3.1107C_f^{0.3102} \quad (8)$$

Therefore, the chloride binding isotherms of hydrated phases for a certain cementitious material can be predicted using the following equation

$$C_b = \sum_{i=C-S-H,AFm,HT} (f_{b_i} \cdot C_{b_i}) \quad (9)$$

Where the f_{b_i} is the mass fraction of C-S-H, AFm, and hydrotalcite phases in the hydration products; C_{b_i} is the bound chloride in each hydrated phase calculated using Eq.s (6)-(8).

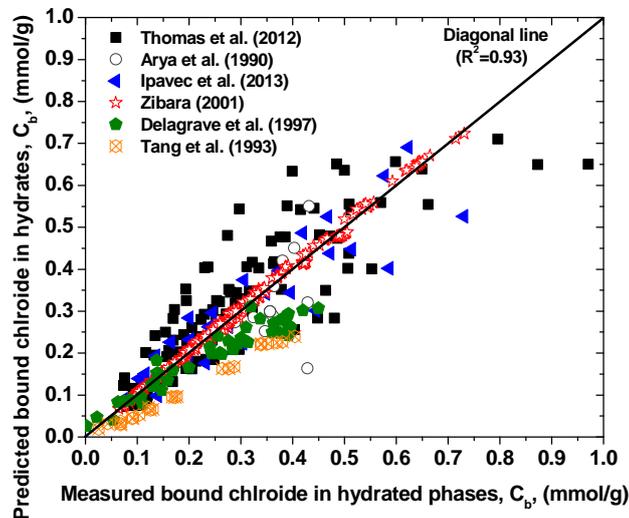


Fig. 3 Comparison of binding capability of hydrated phases predicted using the proposed equation and experimental data from literature

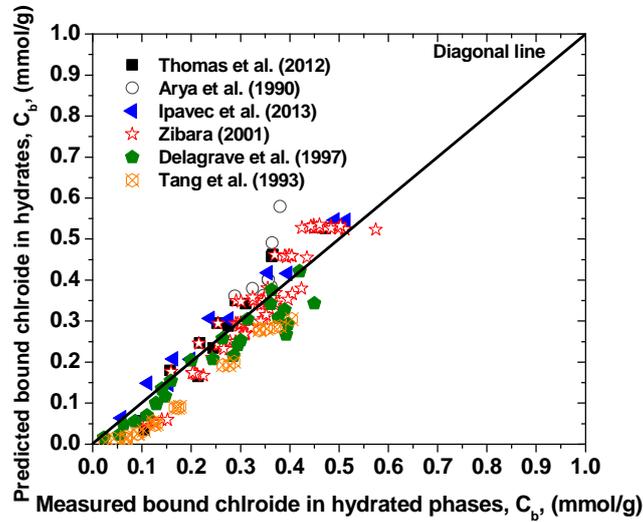
3. Discussion

3.1 Verification and comparison with other predictive models

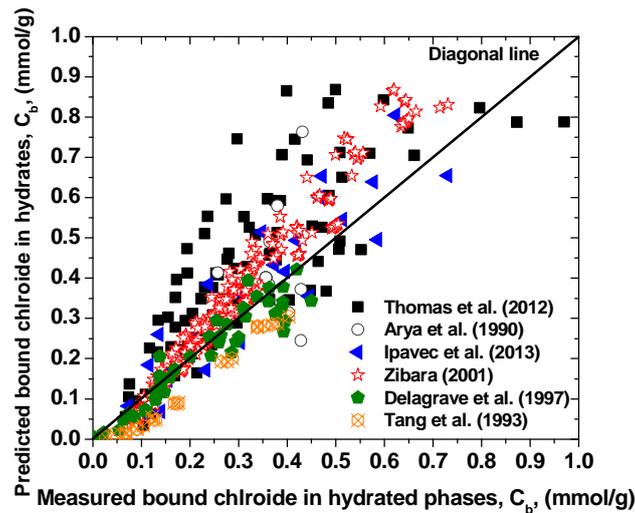
Fig. 3 shows the comparison of binding capability of hydrated phases predicted using the proposed equation and the experimental data from literature. The coefficient of determination is about 93%, indicating the proposed model can reasonably represent the chloride binding isotherms of blended cements. Due to the dominant weighting of data from Zibara (Zibara 2001), the predicted value fits perfectly with the experimental data. For the data from other sources, the predicted model can either slightly overestimate or underestimate the chloride binding capabilities of blended cements.

Hirao *et al.* proposed an equation to calculate the binding isotherms of OPC based on the binding isotherms of the C-S-H and AFm phases (referred as Hirao model) (Hirao *et al.* 2005). The proposed equation was verified for pure OPC system, but its applicability to blended cements is unknown. However, if the C-S-H and AFm phases are the only two dominant phases that contribute to the binding capability in blended cements, this model may provide a reasonable estimation as well. Fig. 4 shows the comparison of binding capability of hydrated phases measured in literature and that predicted using Hirao model. It can be seen that for pure OPC system, Hirao model is in good agreement with the experimental data. This strong agreement indirectly implies that the estimation of phase assemblage using thermodynamic calculation is reasonable. However, for blended cements, the estimation using Hirao model generally overestimates the binding capability.

Fig. 5 shows the comparison of the proposed binding isotherms here and Hirao model for AFm, C-S-H, and hydrotalcite. It can be seen that the binding capability of C-S-H in this study is substantially smaller compared with that of Hirao model. It may indicate that for blended cements, the binding capability is far less dependent on the amount of C-S-H, in comparison to OPC system. In addition, the binding capability of hydrotalcite is found to be 2.0-2.5 times higher than



(a)



(b)

Fig. 4 Comparison of binding capability of hydrated phases measured in literature and that predicted using the Hirao model (a) pure OPC (b) OPC with/without SCMs

that of AFm, which indicates that binding capability of hydroxalite, if it exists in blended cements, cannot be ignored. However, it should be noted that the obtainment of binding isotherms of hydrated phases in this study is through the mathematical regression analysis, which does not have any physical meaning. Nevertheless, the optimized formula for predicting binding isotherm of each hydrate phase shows reasonable trends.

It is well known that the replacement of OPC by blast-furnace slag, or fly ash, or silica fume can increase the amount of C-S-H due to pozzolanic reaction. In addition, the high alumina but little sulfates content in blast-furnace slag and fly ash can potentially increase the AFm phases

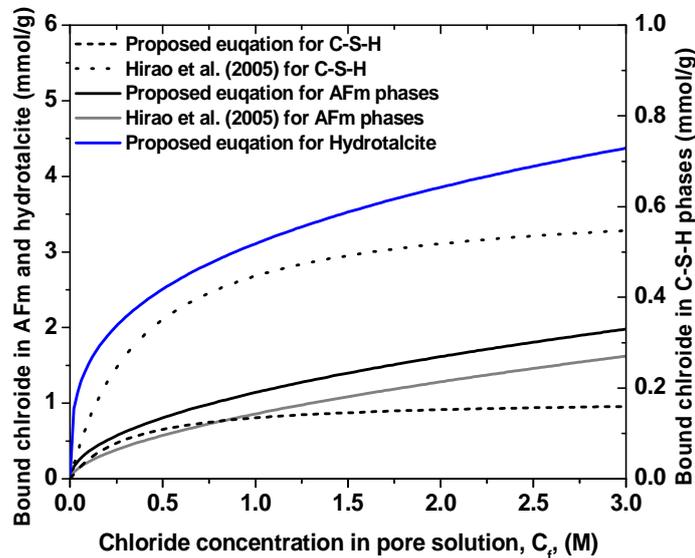


Fig. 5 Comparison of chloride binding isotherms of hydrated phases (i.e., C-S-H, AFm, and hydrotalcite phases) proposed by the present work and Hiraio model

formation (Barbara Lothenbach *et al.*, 2011). Therefore, it is reasonable that the predicted binding capabilities of OPC blended with blast-furnace slag and fly ash, according to the Hiraio model, increase. However, the overestimation of binding capabilities by Hiraio model for blended cements suggests that the binding isotherm of C-S-H is substantially overestimated. On the other hand, silica fume can reduce the chloride binding capability of OPC, although it increases the amount of C-S-H. The reduced binding capacities of silica fume-blended OPC can be attributed to the dilute effects of clinker, which reduces the proportion of both AFm and hydrotalcite phases. It indirectly supports the argument that the binding capability of blended cement is less dependent on the amount of C-S-H. Therefore, in the case of pure OP, the currently proposed model and Hiraio model are comparable, and both in good agreement with experiments. However, in term of blended cements, the proposed model seems to be more reliable while Hiraio model generally overestimates the binding capability.

The proposed equation was implemented to predict the binding capability of hydrated phases in ten different cements reported by Baroghel-Bouny *et al.* (2012) which was initially not included in the model development. It can be seen from Fig. 6 that the predicted value matches the experimental data reasonably. The error of source of the proposed model can from (i) the insufficient estimation of hydrated phase assemblage (e.g. carbonate-bearing phases) for cements, (ii) optimization process as it has little physical meaning, and (iii) inadequate consideration of all the chloride binding phases and its corresponding mechanism.

3.2 Comparison with the isotherms measured by potentiometric titration

It should be emphasized that the current model was established according to the isotherm data measured using ‘equilibrium method’. In term of service-life prediction of existing infrastructure, the predicted chloride binding isotherms may not reasonably represent the binding behaviors of in-

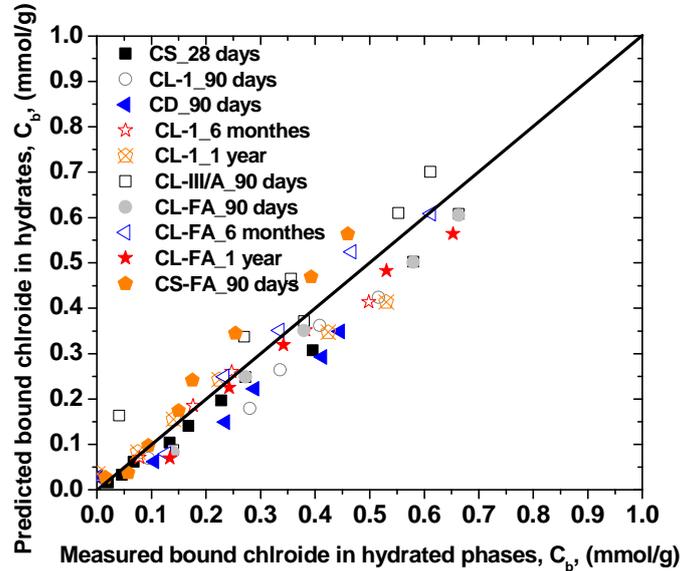


Fig. 6 Comparison of binding capability of hydrated phases measured by Baroghel-Bouny *et al.* (Baroghel-Bouny *et al.* 2012) and that predicted using the equation proposed in this study

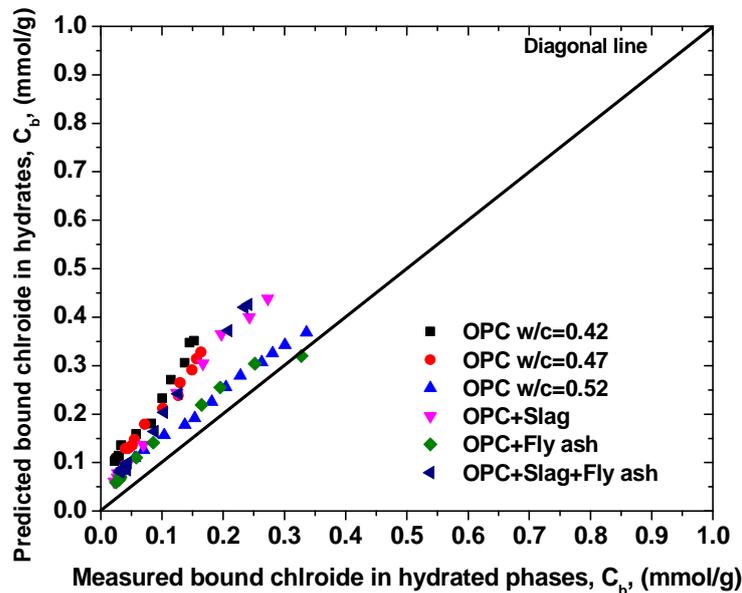


Fig. 7 Comparison of binding capability of hydrated phases measured using potentiometric titration methods and predicted using the proposed method

service concrete due to the non-equilibrium state of binding behaviors. A more representative way to characterize the chloride binding capability of concrete is to measure the free and bound chloride content after performing the diffusion or migration tests. For concrete exposed to non-

saturated condition (i.e. drying-wetting cycles), the chloride binding behavior may not reach equilibrium state even after a long-term exposure (Ye *et al.* 2013). Therefore, the direct implementation of the proposed models may provide misleading results for service-life prediction. Fig. 7 shows the comparison of chloride binding capability of cements measured using potentiometric titration methods and predicted using the proposed method. The cements were exposed to a cyclic drying-wetting chloride-bearing atmospheric condition for six months. The water and acid-soluble chloride contents were collected and measured using potentiometric titration method, to represent the free and total chloride content in cements. The details of the experiment can be found in the research of Chen (Chen 2016). It can be seen that the chloride binding capability measured using potentiometric titration method after exposed to salt-fog drying-wetting cycles is generally smaller than that predicted using the present model. The study implicates the non-equilibrium state of chloride binding behavior for cements exposed to cyclic drying-wetting conditions. In addition, 'equilibrium method' may also overestimate the binding capability due to the larger exposure surface area for grinded particles, which may absorb excessive chloride ions than bulk samples.

4. Conclusions

In this paper, a new predictive model for chloride binding isotherms of blended cements was proposed. Hundreds of data points from seven different sources regarding the chloride binding isotherms of pure OPC and OPC blended with various SCMs were selectively collected. The hydrated phase assemblage of each cement was estimated using thermodynamic calculation based on the mixing proportion, chemical composition of reactants, and degree of hydration. The binding isotherms of main hydrated phases including AFm, C-S-H, and hydrotalcite, were regressed using optimization algorithm. The proposed model has been compared with the model suggested by other researchers, and verified using the data from a different source. Following conclusions can be drawn based on this study

- The proposed model can reasonably predict the chloride binding isotherms of blended cements.
- A new formula to estimate the binding isotherms of hydrated phases, including C-S-H, AFm, and hydrotalcite, was suggested. It shows that the chloride binding capability of hydrotalcite can be up to 2.0-2.5 times of that of AFm phases.
- Langmuir-type isotherm model shows the best fitting to the chloride binding isotherms of the hydrated products of pure OPC over the range of 0-3M.
- For pure OPC, the proposed model provides a comparatively estimation as Hirao model. However, for blended cement, the Hirao model seems to overestimate the binding capabilities.
- For blended cements, the chloride binding capability is less dominated by the amount of C-S-H, as compared to pure OPC.
- When exposed to a cyclic drying-wetting condition, the chloride binding behavior of cement is in a non-equilibrium state. Therefore, the direct implementation of the proposed model may overestimate the chloride binding capability during service-life prediction.

5. Appendix collected data from literature for model development

Table A1 The data implemented in the development of a predictive models for chloride binding isotherms in cementitious materials

Sources	Mixture ID in literature	Mixture proportion ^a	Water-to-binder ratio	Age (M)	Number of points	
Thmoas <i>et al.</i> (2012)	OPC	100% OPC	0.50	9.0	7	
	OPC	100% OPC	0.30	9.0	7	
	8SF	92% OPC+8% SF	0.50	9.0	7	
	8SF	92% OPC+8% SF	0.30	9.0	7	
	8SF(2)	92% OPC+8% SF	0.50	2.0	3	
	8MK	92% OPC+8% MK	0.50	9.0	3	
	8MK	92% OPC+8% MK	0.30	9.0	6	
	8MK(2)	92% OPC+8% MK	0.50	2.0	3	
	25SL	75% OPC+25% SL	0.50	9.0	7	
	25SL	75% OPC+25% SL	0.30	9.0	7	
	25FA	75% OPC+25% FA	0.50	9.0	7	
	25FA	75% OPC+25% FA	0.30	9.0	7	
	25FA(2)	75% OPC+25% FA	0.50	2.0	3	
	25SL/6SF	69% OPC+6% SF+25% SL	0.50	9.0	7	
	25SL/6SF	69% OPC+6% SF+25% SL	0.30	9.0	7	
	25FA/6SF	69% OPC+6% FA+25% SL	0.50	9.0	7	
	25FA/6SF	69% OPC+6% FA+25% SL	0.30	9.0	7	
	25FA1	75% OPC+25% FA	0.50	9.0	3	
	Arya <i>et al.</i> (1990)	OPC1	100% OPC	0.50	1.0	1
		30% PFA	70% OPC+30% FA	0.50	1.0	1
70% GGBS		30% OPC+70% SL	0.50	1.0	1	
10% CSF		90% OPC+10% SF	0.50	1.0	1	
SRPC		100% OPC	0.50	1.0	1	
OPC1		100% OPC	0.40	1.0	1	
OPC1		100% OPC	0.50	1.0	1	
OPC1		100% OPC	0.60	1.0	1	
OPC1		100% OPC	0.50	1.0	1	
OPC1		100% OPC	0.50	1.9	1	
OPC1		100% OPC	0.50	3.7	1	
OPC1		100% OPC	0.50	1.9	1	
OPC1		100% OPC	0.50	2.1	1	
OPC1		100% OPC	0.50	2.8	1	
OPC1		100% OPC	0.50	3.7	1	
OPC1		100% OPC	0.50	4.7	1	
OPC1		100% OPC	0.50	2.9	1	
OPC1		100% OPC	0.50	3.7	1	
OPC1		100% OPC	0.50	5.6	1	

Ipavec <i>et al.</i> (2013)	100C	100% OPC	0.45	5.3	6
	70C-15S-15A	70% OPC+15% FA+15% SL	0.45	5.3	6
	70C-30S	70% OPC+30% SL	0.45	5.3	6
	70C-30A	70% OPC+30% FA	0.45	5.3	6
	85C-15SF	85% OPC+15% SF	0.45	5.3	6
Zibara (2001)	Control	100% OPC	0.30	2.0	7
	Control	100% OPC	0.30	2.0	6
	8SF	92% OPC+8% SF	0.30	2.0	7
	8SF	92% OPC+8% SF	0.30	2.0	7
	25SL	75% OPC+25% SL	0.30	2.0	7
	25SL	75% OPC+25% SL	0.30	2.0	7
	40SL	60% OPC+40% SL	0.30	2.0	7
	25FA	75% OPC+25% FA	0.30	2.0	7
	25FA	75% OPC+25% FA	0.30	2.0	7
	40FA	60% OPC+40% FA	0.30	2.0	7
	8MK	92% OPC+8% MK	0.30	2.0	6
	25SL6SF	69% OPC+6% SF+25% SL	0.30	2.0	7
	40SL5SF	55% OPC+5% SF+40% SL	0.30	2.0	7
	25FA6SF	69% OPC+6% SF+25% FA	0.30	2.0	7
	40FA5SF	55% OPC+5% SF+40% FA	0.30	2.0	7
	Control	100% OPC	0.50	2.0	3
	8SF	92% OPC+8% SF	0.50	2.0	4
	8MK	92% OPC+8% MK	0.50	2.0	4
	25FA	75% OPC+25% FA	0.50	2.0	3
	25FA1	75% OPC+25% FA	0.50	2.0	3
	25FA2	75% OPC+25% FA	0.50	2.0	3
	Control	100% OPC	0.50	9.0	7
	25FA	75% OPC+25% FA	0.50	9.0	7
	25SL	75% OPC+25% SL	0.50	9.0	7
	25FA6SF	69% OPC+6% SF+25% FA	0.50	9.0	7
	25SL6SF	69% OPC+6% SF+25% SL	0.50	9.0	7
	8SF	92% OPC+8% SF	0.50	9.0	7
	Control	100% OPC	0.50	9.0	3
	8MK	92% OPC+8% MK	0.50	9.0	3
	Control	100% OPC	0.50	2.0	7
	Control	100% OPC	0.50	2.0	7
	Control	100% OPC	0.50	2.0	7
Control	100% OPC	0.50	2.0	7	
Control	100% OPC	0.50	2.0	3	
8SF	92% OPC+8% SF	0.50	2.0	3	
8MK	92% OPC+8% SF	0.50	2.0	3	

	Control	100% OPC	0.50	2.0	3
	8SF	92% OPC+8% SF	0.50	2.0	3
	8MK	92% OPC+8% SF	0.50	2.0	3
	Control	100% OPC	0.50	18.0	11
	Control	100% OPC	0.50	18.0	11
	8SF	92% OPC+8% SF	0.50	18.0	11
	8MK	92% OPC+8% MK	0.50	18.0	9
	8MK	92% OPC+8% MK	0.50	18.0	8
	25FA	75% OPC+25% FA	0.50	18.0	9
	25FA	75% OPC+25% FA	0.50	18.0	10
Delagrave <i>et al.</i> (1997)	P25Q3	100% OPC (ASTM Type III)	0.25	- ^b	7
	P25Q3SF	94% OPC+6% SF	0.25	- ^b	9
	P45Q1	100% OPC (ASTM Type I)	0.45	- ^b	8
	P45Q1SF	94% OPC+6% SF	0.45	- ^b	9
	P45Q5	100% OPC (ASTM Type V)	0.45	- ^b	10
Tang <i>et al.</i> (1993)	OPC paste	100% OPC	0.40	2.0	9
	OPC paste	100% OPC	0.60	2.0	6
	OPC paste	100% OPC	0.80	2.0	5
Baroghel-Bouny <i>et al.</i> (2012)	CS	100% OPC	0.5	1.0	7
	CL-1	100% OPC	0.5	3.0	5
	CD	100% OPC	0.5	3.0	6
	CL-1	100% OPC	0.5	6.0	5
	CL-1	100% OPC	0.5	12.0	6
	CL-III/A	100% OPC	0.5	3.0	5
	CL-FA	70% OPC+30% FA	0.5	3.0	5
	CL-FA	70% OPC+30% FA	0.5	6.0	5
	CL-FA	70% OPC+30% FA	0.5	12.0	5
	CS-FA	70% OPC+30% FA	0.5	1.0	8

Notes: a: OPC represents ordinary portland cement, SF represents silica fume, FA represents fly ash, SL represents blast-furnace slag, MK represents metakaolin.

b: The degree of hydration for each mixture in this reference has already been provided, therefore no estimation is needed.

Acknowledgements

The financial support from the National Basic Research Program (Grant No. 2015CB655103), of the People's Republic of China and the National Natural Science Foundation (Grant Nos. 51578497, 51320105013 and 51478419) is gratefully acknowledged.

References

- Amey, S.L., Johnson, D.A., Miltenberger, M.A. and Farzam, H. (1998), "Predicting the service life of concrete marine structures: an environmental methodology", *ACI Struct. J.*, **95**(2), 205-214.
- Angst, U., Elsener, B., Larsen, C.K. and Vennesland, Ø. (2009), "Critical chloride content in reinforced concrete-a review", *Cement Concrete Res.*, **39**(12), 1122-1138.
- Arya, C., Buenfeld, N. and Newman, J. (1990), "Factors influencing chloride-binding in concrete", *Cement Concrete Res.*, **20**(2), 291-300.
- Arya, C. and Xu, Y. (1995), "Effect of cement type on chloride binding and corrosion of steel in concrete", *Cement Concrete Res.*, **25**(4), 893-902.
- Baroghel-Bouny, V., Wang, X., Thiery, M., Saillio, M. and Barberon, F. (2012), "Prediction of chloride binding isotherms of cementitious materials by analytical model or numerical inverse analysis", *Cement Concrete Res.*, **42**(9), 1207-1224.
- Boulfiza, M., Sakai, K., Banthia, N. and Yoshida, H. (2003), "Prediction of chloride ions ingress in uncracked and cracked concrete", *ACI Mater. J.*, **100**(1).
- Brouwers, H. (2004), "The work of Powers and Brownard revisited: Part 1", *Cement Concrete Res.*, **34**(9), 1697-1716.
- Castellote, M., Andrade, C. and Alonso, C. (1999), "Chloride-binding isotherms in concrete submitted to non-steady-state migration experiments", *Cement Concrete Res.*, **29**(11), 1799-1806.
- Chen, W. (2016), "Study on chloride binding and transportation of mortars in salt-fog wetting-drying environments (in Chinese)", (Master of Science), Zhejiang University.
- De Weerd, K., Orsáková, D. and Geiker, M. (2014), "The impact of sulphate and magnesium on chloride binding in Portland cement paste", *Cement Concrete Res.*, **65**, 30-40.
- Delagrave, A., Marchand, J., Ollivier, J.P., Julien, S. and Hazrati, K. (1997), "Chloride binding capacity of various hydrated cement paste systems", *Adv. Cement Mater.*, **6**(1), 28-35.
- Florea, M. and Brouwers, H. (2012), "Chloride binding related to hydration products: Part I: Ordinary Portland Cement", *Cement Concrete Res.*, **42**(2), 282-290.
- Fu, C., Jin, X., Ye, H. and Jin, N. (2015), "Theoretical and experimental investigation of loading effects on chloride diffusion in saturated concrete", *J. Adv. Concrete Tech.*, **13**(1), 30-43.
- Hirao, H., Yamada, K., Takahashi, H. and Zibara, H. (2005), "Chloride binding of cement estimated by binding isotherms of hydrates", *J. Adv. Concrete Tech.*, **3**(1), 77-84.
- Ipavec, A., Vuk, T., Gabrovšek, R. and Kaučič, V. (2013), "Chloride binding into hydrated blended cements: The influence of limestone and alkalinity", *Cement Concrete Res.*, **48**, 74-85.
- Kayali, O., Khan, M. and Ahmed, M.S. (2012), "The role of hydrotalcite in chloride binding and corrosion protection in concretes with ground granulated blast furnace slag", *Cement Concrete Compos.*, **34**(8), 936-945.
- Kulik, D., Berner, U. and Curti, E. (2003), "Modelling chemical equilibrium partitioning with the GEMS-PSI code", PSI Scientific Report, **4**, 109-122.
- Lee, M.K., Jung, S.H. and Oh, B.H. (2013), "Effects of carbonation on chloride penetration in concrete", *ACI Mater. J.*, **110**(5).
- Loser, R., Lothenbach, B., Leemann, A. and Tuchschnid, M. (2010), "Chloride resistance of concrete and its binding capacity-Comparison between experimental results and thermodynamic modeling", *Cement Concrete Compos.*, **32**(1), 34-42.
- Lothenbach, B. and Gruskovnjak, A. (2007), "Hydration of alkali-activated slag: thermodynamic modelling", *Adv. Cement Res.*, **19**(2), 81-92.
- Lothenbach, B., Scrivener, K. and Hooton, R. (2011), "Supplementary cementitious materials", *Cement Concrete Res.*, **41**(12), 1244-1256.
- Luo, R., Cai, Y., Wang, C. and Huang, X. (2003), "Study of chloride binding and diffusion in GGBS concrete", *Cement Concrete Res.*, **33**(1), 1-7.
- Martín-Pérez, B., Zibara, H., Hooton, R. and Thomas, M. (2000), "A study of the effect of chloride binding on service life predictions", *Cement Concrete Res.*, **30**(8), 1215-1223.
- Mien, T.V., Nawa, T. and Stitmannathum, B. (2014), "Chloride binding isotherms of various cements basing on binding capacity of hydrates", *Comput. Concrete*, **13**(6), 695-707.

- Mien, T.V., Stitmannathum, B. and Nawa, T. (2009), "Simulation of chloride penetration into concrete structures subjected to both cyclic flexural loads and tidal effects", *Comput. Concrete*, **6**(5), 421-435.
- Neville, A. (1995), "Chloride attack of reinforced concrete: an overview", *Mater. Struct.*, **28**(2), 63-70.
- Richardson, I. (2008), "The calcium silicate hydrates", *Cement Concrete Res.*, **38**(2), 137-158.
- Sergi, G., Yu, S. and Page, C. (1992), "Diffusion of chloride and hydroxyl ions in cementitious materials exposed to a saline environment", *Mag Concrete Res.*, **44**(158), 63-69.
- Tang, L. and Nilsson, L.O. (1993), "Chloride binding capacity and binding isotherms of OPC pastes and mortars", *Cement Concrete Res.*, **23**(2), 247-253.
- Thomas, M., Hooton, R., Scott, A. and Zibara, H. (2012), "The effect of supplementary cementitious materials on chloride binding in hardened cement paste", *Cement Concrete Res.*, **42**(1), 1-7.
- Vu, K.A.T. and Stewart, M.G. (2000), "Structural reliability of concrete bridges including improved chloride-induced corrosion models", *Struct. Safe.*, **22**(4), 313-333.
- Yang, Z., Fischer, H. and Polder, R. (2012), *Possibilities for improving corrosion protection of reinforced concrete by modified hydrotalcites-a literature review Advances in Modeling Concrete Service Life (pp. 95-105)*, Springer.
- Ye, H., Fu, C., Jin, N. and Jin, X. (2015), "Influence of flexural loading on chloride ingress in concrete subjected to cyclic drying-wetting condition", *Comput. Concrete*, **15**(2), 183-198.
- Ye, H., Jin, N., Jin, X. and Fu, C. (2012), "Model of chloride penetration into cracked concrete subject to drying-wetting cycles", *Constr. Build. Mater.*, **36**, 259-269.
- Ye, H., Jin, X., Fu, C., Jin, N., Xu, Y. and Huang, T. (2016), "Chloride penetration in concrete exposed to cyclic drying-wetting and carbonation", *Constr. Build. Mater.*, **112**, 457-463.
- Ye, H., Tian, Y., Jin, N., Jin, X. and Fu, C. (2013), "Influence of cracking on chloride diffusivity and moisture influential depth in concrete subjected to simulated environmental conditions", *Constr. Build. Mater.*, **47**, 66-79.
- Zibara, H. (2001), "Binding of external chlorides by cement pastes", Ph.D. Thesis, University of Toronto.
- Zibara, H., Hooton, R., Thomas, M. and Stanish, K. (2008), "Influence of the C/S and C/A ratios of hydration products on the chloride ion binding capacity of lime-SF and lime-MK mixtures", *Cement Concrete Res.*, **38**(3), 422-426.