As chloride ions ingress into cement-based composites, the service life of the cementitious materials will be negatively affected when the part overloading the content threshold of chloride ion can not be bound by hydrated products in cement-based materials. This paper doesn’t only indicate the chloride binding capability as well as the various effects of comprehensive influential factors correspondingly. But it also elucidates different chloride binding mechanisms of various cement matrix materials. In addition, the relationship between chloride binding and chloride permeability was also reconsidered in this paper. Especially, for the prediction to service life-span of reinforced concrete structures with chlorination, the authors reflect on the contribution of the chloride binding. Ultimately, on the basis of considerable significant existing researches some vital issues and challenges with relevant countermeasure are proposed by the authors.

Key-words : Chloride binding, Cement-based material, Chloride diffusion, Chloride migration, Durability, Prediction of service life

1. Introduction

Chloride ions might be one of the primary factors accounting for the deterioration of reinforced concrete structures. Especially when cementitious materials indwell excessive chlorine, as well cement-based materials long-time serve in chloride environment.¹⁻³ Cement-based composites will be eroded by chloride ions only the chloride ion (Cl⁻) concentration in pore solution reaches a certain threshold.⁴⁻⁵ Namely, the ratio of chloride ions concentration to hydroxide ions (OH⁻) concentration is higher than 0.60% (Cl⁻·OH⁻ > 0.60%).¹⁻² In order to facilitate engineering application, the limit value³ on Cl⁻ of concrete stipulated by American concrete institute is 0.1 wt % of cement (0.06 wt % of prestressed concrete), while the limit value on Cl⁻ stipulated by Japan is 0.3–0.6 kg Cl⁻·m⁻³ concrete. So improving the resistance to chloride ion erosion of cementitious materials is deemed as the pivotal of delaying chloride transmission rate, besides reducing the internal chlorine ion concentration. Fortunately, if the major of chloride ions can be bound under the physicochemical effect, rather than existing as free chloride ions in the chloride penetration process. Meanwhile because bound chloride can block some pores, it’s conducive to restrict the penetration rate by increasing the compactness of cement matrix materials, in return that will limit the invasion of external chlorine.⁴⁻⁵ Thus for, the chloride binding ability has an indispensable contribution to the enhancement of durability to extend the service life of concrete structures.⁶⁻⁸

Overall there are two kinds of approaches to improving the durability of cement-based composites in chlorination environment. On one thing, it can be fulfilled by weakening chloride permeability of cement-based composites. On the other, improving the capacity of binding chloride ions can reduce the chloride concentration of pore aqueous solution dramatically, particularly the free chloride concentration.⁵⁻⁹,¹⁰ In terms of anti-permeability, it’s essential for cementitious materials to equip the compactness with the refined aperture-structure.⁹⁻¹² But in some situations for cement-based materials, there still exists redundant chloride ions overrunning the range of chloride concentration threshold unavoidably.⁴⁻⁵,¹³ As for the chloride ions contained into cement-based materials, high resistance to chloride corrosion generally are supported by low water-cement ratio and well-selected components of cement matrix materials respectively. That means marine sand, some mineral and chemical admixtures containing with chloride confront certain limitations in employment as cement components, just as the application of chlorinated deicing salt¹⁴,¹⁵ in external environment. However, chloride binding capability of cement matrix can effectively lift these restrictions triggering relevant resource
shortage. The indispensable value of chloride binding in engineering application reveals that it makes significant sense to explore the progress of study on chloride binding capability of cement-based materials. By the way, compared with the first approach, the latter relevant studies is lack of further researches and discussion evidently. So it’s a burning issue to grasp the progress on chloride binding capability of cement-based material by backing up preceding research in the field.

As previous study has presented, chloride binding capacities of cement materials ascribes to diverse factors. For one aspect, there are some internal reasons of cement matrix, such as water-binder ratio, the type and dosage of cement17)–20) the incorporation with different mineral additives and chemical admixtures and so on. From another view, likewise various external aspects make vital influence on the chloride binding capability. For example, multiple service environments couple with chlorine salts3),13),21) impose varying curing regimes,11) different experimental and testing methods and so on.12)–22)

Centering on the effect of exposure temperature on chloride binding capability, the effects on cementitious materials with mineral supplementary exerted by temperature are much complex. Extensive researches indicated that ascending curing temperature leads to the descending chloride binding capability. As Y. Yan23) proposed that the curing high temperature can reduce the quantity of Friedel’s salt in metakaolin (MK)-cement so that chemically chloride binding capacity is reduced as the increasing temperature. However, D. K. Panesar and S. E. Chidiac14) replaced the equal amount of cement with ground granulated blast furnace slag (GGBFS) by 0–60% in different temperature (3–22°C). The results presented the order of chloride-binding capability corresponding to exposure temperature was: 5°C < 13°C < −3°C < 22°C. Namely the higher temperature will company with higher chloride binding capability in the range of 0–22°C, which was similar as O. R. Ogirigbo, L. Black et al.24) recognized. What’s more, the experiment turned out that the more incorporation of GGBFS can improve the chloride binding capability of cement matrix composites better. Indeed, diverse mineral supplementaries play disparate roles in chloride binding ability of cement matrix materials.

It has been admitted that the amount of bound chloride ascends along with the developing hydration degree of cementing materials. And chloride ions are bound in the initial stage of hydration primarily, while in the late stage cementing materials. And chloride ions are bound in the ascends along with the developing hydration degree of chloride binding ability of cement matrix materials. Diverse mineral supplementaries play disparate roles in improving capability of cement matrix composites better. Indeed, incorporation of GGBFS can improve the chloride binding capacity.

What’s more, the experiment turned out that the more incorporation of GGBFS can improve the chloride binding capability of cement matrix composites better. Indeed, diverse mineral supplementaries play disparate roles in chloride binding ability of cement matrix materials.

2. The chloride binding capability of different cement-based materials

Generally auxiliary materials of cement matrix materials can be classed into chemical additives and mineral admixture. Furthermore, opposite to chemical admixture, mineral supplementary prefer to make influence on chemical chloride binding instead of physical chloride binding. Other than those supplementaries, the chloride binding abilities of cement-based materials results from multiple types of cement.17)–20) Whatever mineral admixtures are incorporated with diversified cement, there are three index commanded the chloride binding capability: calcium-to-alumina ratio (C/A), calcium-to-silica ratio (C/S) and silica-to-alumina (S/A). This conclusion has been confirmed by A. Dousti, J. J. Beaudoin et al.30) that the lower of the C/S ratio of the C–S–H can lead to the decrease of bound chloride ions. More important, the content of sulphate in cement-based materials is a nonnegligible factor for chloride binding, as well as active aluminium oxide (Al2O3) and silicon dioxide (SiO2).
 Chemical admixtures have been regarded as the sixth constituent of concrete, which make momentous contributions to the work-ability, mechanical performance and durability of cement-based materials. Nevertheless, the attendant influences of different chemical admixtures on chloride binding in cementitious composites remain to be waiting for further studies. In a minority of available researches, the chemical admixtures were set as the central objects of studies. The results of those studies declared the complex impacts on chloride binding capacity of cementitious composites. For instance, on the basis of the Freundlich isotherm and Langmuir isotherm, Feng Wei et al. proposed a ‘Electrical Double Layer’ model to portray the effect of polycarboxylate superplasticizer on chloride binding capability in cement paste. Their results concluded that the initial rate of binding chloride ion decreased with the increasing content of polycarboxylate superplasticizer. In essence, chloride-ion adsorbent is similar with rust inhibitor, which is supposed to possess quick and stable effect as well as small required dosage and so on. And it should be in the context of negligible influence on other properties of reinforcement cement matrix construction, when chloride-ions adsorbent gives raise to the excellent chloride binding capability. Song Qiming and Peng Gaifei et al. measured the content of chloride incorporated with mortar, in addition, they also conducted the electric flux test complying with ASTM C1202 to estimate anti-permeability. The data of their experiments showed that when the Cl⁻-Agent [3CaO·Al₂O₃·Ca(NO₂)₂·nH₂O] was incorporated by 6 wt% of cement, the chloride binding capability increased greatly due to the Cl⁻-Agent with high-efficiency chloride adsorption. Indeed, the Cl⁻-Agent can absorb some free chloride ions released from bound chloride ions, as same as Cl⁻-Agent can bind never absorbed chloride to form Friedel’s salt. When Cl⁻-Agent worked, nitrite ions (NO₂⁻) was replaced by the free chloride ions and gradually regenerated calcium nitrite by reacting with hydrated calcium aluminates in cementitious materials. The chemical reaction equation for recycling is as follows:

\[
3\text{CaO}·\text{Al}_2\text{O}_3·\text{Ca(NO}_2)_2·n\text{H}_2\text{O} + 2\text{Cl}^- \rightarrow 2\text{NO}_2^- + 3\text{CaO}·\text{Al}_2\text{O}_3·\text{CaCl}_2·n\text{H}_2\text{O}.
\]

Some other chloride adsorbents exert their functions based on the similar mechanism of adsorbing chloride ions as above, i.e., ion exchange mechanism. Exactly as layered double hydroxides (LDHs) is a typical representative of diverse chloride adsorbents. Thereinto, Y. X. Chen, Z. H. Shui et al. exploited the chloride binding capability of Ca–Al–NO₃ LDHs in simulated pore solution of hardened cementitious materials. According to the experimental results, the maximum chloride adsorption capacity can be up to 3.38 mM/L, which showed the outstanding effect of LDHs in chloride binding. In addition, the experiments indicated that chloride binding of cement paste with LDHs accorded with the model of Langmuir isotherm adsorption.

J. X. Xu, W. Feng et al. investigated the influences of three kinds of surfactants on chloride binding ability of cement paste. The three types of surfactant: TEA-Lauryl sulfate (TEALS), sodium dodecyl benzene sulfonate (SDBS) and decyl-polyglucoside (DPG) in sequence were regarded as the represent of cationic surfactant, anionic surfactant and anionic surfactant respectively. In the results basing on chloride adsorption isotherm of cement paste with surfactant and the control group (the specimens without surfactant), TEALS was conducive to chloride binding, but the SDBS and DPG conducted negative impact. The results manifested that cement-based materials have higher adsorption rates with the cationic surfactant rather than anionic surfactant. The reason is that theoretically cationic surfactant can transform the zeta potential of cement particles surface from negative to positive, which is beneficial to the physically absorbing chloride ions with negative charge based on the electrostatic force. On the contrary, the adsorption of anionic surfactant to cement particles enhances the negative zeta potential which leads to the increasing repulsive force between the cement surface and chloride ions with negative charge. Therefore, the amount of physically bound chloride ions can be reduced by anionic surfactant. Different with those two types of surfactant, the non-ionic surfactant is not almost absorbed by cement matrix, so the zeta potential on the surface of cement doesn’t change regardless of whose negative influence on chloride binding. In addition the process forming technology also might alter the chloride binding capability. Because there are competitions between partial ions of surfactant intensely and some ions of cementitious materials on the hydration reaction, the way of incorporation of surfactant is one factor impact the chloride binding capability of cement-based materials. The investigation covered if the surfactant is incorporated in blender at last, then its effect on chloride binding will be cut down as much as. Similar with other chemical admixtures, compared with Langmuir isotherm, Freundlich isotherm shows a better portrait for the effects of cement-based materials with the different surfactant binding chloride, as shown in Fig. 1. exhibited.

2.2 Chloride binding capability of cement matrix with mineral admixtures

Numerous mineral auxiliary of cementitious materials aren’t just only substitutions of cement, but can reinforce the durability of cement matrix generally. In especial, there are several active mineral admixtures containing activated alumina and/or activated silicon dioxide: fly ash (FA),(12),(41),(42) pozzolana,(43)–(45) granulated blast furnace slag (GBFS) and steel slag,(44)–(45) MK,(46)–(49) natural zeolite (NZ),(50) and so on.(51) Those play indispensable roles in chemically binding capability of cement-based materials. Whereas, not all mineral admixtures are favorable for curing chloride ions. Just as the research of M. V. A. Florea et al. and T. Y. Pan et al. showed that C/S of C–S–H gel in hardened cement slurry with silica fume decreased as the hydration of C–S–H, even when there was still calcium
hydroxide in the cement slurry. Namely, the chloride binding capability was reduced ascribe to the existence of silica hydroxide in the cement slurry. Namely, the chloride binding capability increased as the increasing content of Fridel salt as well as C slag.64) The content and types of calcium sulfate54) and types of magnesium sulfate65) are so too. 2.2.1 Single component mineral supplementary 2.2.1.1 Active mineral admixture Q. Cao, K. F. Tan et al.26) has demonstrated that the rank in contributions of mineral admixtures to chloride binding capability from high to low is MK, GBFS and steel slag, FA, as As illustrated in Fig. 2. Where, \( C_b \): the chloride capacity of various mineral supplementary.

According to the results obtained by M. D. A. Thomas and R. D. Hooton et al.,55) the pastes with meta-kaolin (45% \( \text{Al}_2\text{O}_3 \)) showed the best chloride binding capability while the pastes with silica fume (<0.5% \( \text{Al}_2\text{O}_3 \)) had the lowest. Y. Yan23) reported that when the meta-kaolin at the dosage in range of 0–40% equally substitute for partial cement, the chloride binding capability increased as the increasing dosage of meta-kaolin, which due to the increasing content of Fridel’s salt as well as C–S–H gel in the hydration system of metakaolin-cement materials. As D. K. Panesar and S. E. Chidiac15) stated that the chloride binding capability is responsible for the microstructure of harden concrete mixed with GGBFS, especially for the positive affect on aperture-structure. On the another, the chloride concentration is also a significant factor causing the alteration on the ratio of chemically bound chloride ions as the same as physically bound chloride ions. In general, the percentage of chemically bound chloride ions is elevated more much with the higher chloride concentrations. For the cement blended with 40% GGBFS, when the chloride concentration increased from 0.5 to 1.0 mol/L or more, the chemically chloride binding capability gradually occupied dominant position in the total chloride binding capacity.

M. Saillio, V. B. Baroghel et al.58) manifested that minor of active supplementary cement materials (SCMs) participated in the formation of ettringite (Aft) phases, while active aluminium of the high active SCMs might substitute for silicium in C–S–H and even anhydrous phases. In sodium chloride solution of high concentration, physically binding chloride is dominant instead of chemical chloride binding. In addition, physical binding capacity can be improved with the content of SCMs in cement paste, which principally arises from the different types of C–S–H production during hydration of cement pastes with SCMs. However, the higher calcium-silicon ratio of C–S–H gel brings along the more remarkable the binding capacity with chloride ions. On the opposite side, it should be noted that the participation of active mineral admixtures can reduce the calcium-silicon ratio of C–S–H gel generally, thus the physical chloride binding capacity of C–S–H decreased correspondingly.

2.2.2 The compound mineral admixtures

Interestingly, the multi-component of mineral admixtures usually can more significantly reinforce the chloride binding property of cementitious composites than single component of mineral supplementary, based on the mutual synergy in pozzolanic effect,26,55,68) morphological effect,35,57) micro-aggregate filling effect and secondary reaction of hydration.23,26,48) More important, inert mineral supplementary can efficiently descend the sensitivity of active mineral admixture to varying temperature in environment and the hydration heat,14,23,48) if which is compounded with active mineral supplementary.
As for the chloride binding mechanisms of mineral supplementary, in fact mineral admixtures generally absorb chloride ions by impelling the transformation from strätlingite, carbonaluminate and other relevant component of mineral supplementary to Friedel’s salt, Kuzel’s salt as well as homologous hydration products, rather than directly reacting with the free chloride ions in cement-based materials. On the ground of experimental results, clinoptilolite is the main compound of the natural zeolite-lime mixture with high C/A ratio to generate Friedel’s salt in chloride solution with low concentrations. Moreover, the MK-lime mixture with a high C/A ratio can boost the content of the Friedel’s salt, whereas the lower C/A ratio was facilitate to the formation of strätlingite and the higher content of clinoptilolite crystals in the NZ-lime mixture. Therefore, although the capacity of active alumina and silicon dioxide does make a crucial difference on chloride binding but which depends on C/A ratio as well as C/S ratio of mineral admixture in cement matrix composites.

It has been widely recognized that the sulfate can impair the chloride binding ability of cement matrix composites. But, in fact suitable content of sulphate promoted chloride binding capability. Y. Y. Wang, Z. H. Shui et al. resulted that when moderate amount of gypsum exists in the blender of MK-lime and cement, the formations of Ms and ettringite (Af) are accelerated significantly, chloride ions can replace partial OH\(^{-}\) and SO\(_4^{2-}\) of Ms and Af so as to synthesize the Friedel’s salt in a chloride-rich environment. However, addition of 4 and 8 wt % gypsum can reduce 11% of the bound chloride amount. What’s more, extensive experiments has been carried out to confirm the conclusion that the atmospheric carbonation was detrimental to the bound chloride relying on Friedel’s salt, Kuzel’s salt and C–S–H gels in chloroaluminate, giving the descending PH charged of the atmospheric carbonation. H. Ez-zaki and A. Diouri declared that when the partial Portland cement was replaced with treated sediments and shell powders, the corrosion risk of steel-bar was restricted effectively as bound chloride ions increased. Meantime, the free chlorides content decreased in the substituted mortars because of the compacting effect of the fine particles. J. H. Yan and C. Han et al. investigated the glass powder-FA-cement system, the research revealed powdered glass-FA-cement paste has the less physically bound chloride ions and less total bound chloride ions, but more Friedel’s salt than the FA-cement paste, when the two kinds systems contented with equal mass of FA. Indeed, with glass powder accounting for 8% by the weight of cement, the total chloride binding capacity of glass powder-FA-cement specimens was less about 10% than the FA-cement specimens.

Y. Y. Wang and Z. H. Shui et al. probed into the mechanical performances, chloride migration and binding mechanisms of marine mortars with coral waste powder and MK. According to the thermodynamic analysis on the mechanisms of hydrate conversion, chloroaluminate has the outstanding capability to derive Friedel’s salt in chloride-rich environment, and AFm-SO\(_4\) can transform into Friedel’s salt, meanwhile gypsum was released below 21°C. Then the released gypsum further can react with AFm-SO\(_4\) to constitute additional Af-SO\(_4\) after exposed to chloride solution. Moreover, bound chloride content of cement-based materials nearly presents linear relationship with active alumina content of cementitious matrix. Obviously the mineral admixture consisting of coral waste powder and MK improved chloride binding performance of mortars remarkably, which due to the synergetic effect between carboaluminate formation and pozzolanic reaction.

2.3 The function of nano-materials on chloride binding capacity

Based on the equilibrium adsorption of Freundlich isotherm model, Z. Q. Yang and Y. Gao researched the function of nano-Al\(_2\)O\(_3\) (NA) on the chloride binding capacity of cement paste, the results of revealed that the incorporation of NA can advance the chloride binding capacity. It was closely related with the increasing amount of calcium Ms hydrate (AFm) subject to the reaction between nano-Al\(_2\)O\(_3\) and portlandite with gypsum. When cement paste contenting with 5.0% NA were immersed into the 0.05 mol/L NaCl solution, the chloride binding capacity was raised by 37.2% compared with the plain cement paste at 28d. In the whole, when NaCl concentration increased in the range of 0.05–3.0 mol/L, the bound chloride content increased with the increasing dosage of NA, here the NA was designed in the range of 1–5% by the weight of cement. Equivalently, only provided the low dose of NA, the considerable development of chloride binding capability can be obtained. What’s more, the high specific surface of the NA propelled the formation of Friedel’s salt especially when specimens were immersed into NaCl solution of high concentration. Furthermore, the function of nano-materials on the micro-structures of cementitious composites also play a vital role in the chloride binding capability.

2.4 Chloride binding capability of various cement

Compered with other factors exerting effect on chloride binding performance, the type of cement play a crucial role in the chloride binding capability of cement matrix materials. Because varied cement consist of different constituents, additionally cement accounts a large incorporation of cement-based material, divers cement is responsible for disparate chloride binding behaviors. What’s more, in term of composite cement containing mineral mixture, the internal mineral mixture of cement exert the effect on chloride binding capability and mechanisms just as similar as which of the mineral supplementary.

2.4.1 The respective chloride binding capacity of OPC, SAC and AC

J. Geng, J. Y. Sun et al. conducted the study on chloride binding characteristics of three different types of cement, i.e. ordinary Portland cement (OPC), sulphoaluminate cement (SAC) and high alumina cement (AC) at
28d. The consequent results turned out that physical adsorption of calcium silicate hydrated gel (C–S–H) is the major contributor of chloride binding, rather than the chemical binding ascribe to the formation of Friedel’s salt in the cementitious materials with admixed chloride ions. Additionally, with respect to the rates of chloride binding ability at 28d, the best is OPC (23.9%) and then AC (19.97%), the weakest is SAC (7.95%). While in neither SAC or AC the stability of chloride binding weren’t better than the stability in OPC, as the amount of chemically bound chloridion in both SCA and AC were much less than OPC hydration system. In recent years, except for common cements [i.e. Portland cement (P.I; P.II), OPC, SAC and AC], alkali-activated cement and phosphate cement has been paid increasing attention on the more much prominent anti-permeability of phosphate cement to the external chloride ions of service environment.

### 2.4.2 The chloride binding capacity of phosphate cement

As to the study on the resistance to chloride erosion of magnesia-phosphate cement, S. C. Zhen, J. M. Yang et al.\(^{18}\) measured the chloride concentration at different depths to the surface of samples, which were immersed in saturated sodium chloride solution and seawater for about half year as well. The results of the study exhibited that the mechanisms of the resistance to chloride erosion of magnesia-phosphate mortar can be distinguished with which of ordinary cement mortar significantly absolutely. Because there existed tiny conversion from hydroxyapatite [HAP, Ca\(_5\)(PO\(_4\))\(_3\)(OH)] to chlorapatite [Ca\(_5\)(PO\(_4\))\(_3\)Cl]\(^{19}\) nevertheless which meant that more HAP can participate in the formation of physical barrier [e.g. Fe(PO\(_4\)) \(_2\)H\(_2\)O] to inhibit steel corrosion in magnesia-phosphate mortar\(^{20}\) better. Likewise, the other hydrated phosphate [i.e. whitlockite [Ca\(_3\)(PO\(_4\))\(_2\)] and hilgenstockite [Ca\(_4\)O(PO\(_4\))\(_2\)]] make weeny contributions to chloride binding capacity. Evidently, different with ordinary cement, the main contribution of phosphate cement on resistance to chloride erosion mainly is based on the effect of barrier inhibiting steel erosion rather than chloride binding ability. The chloride anti-permeability of phosphate cement is about 2–3 times as that of ordinary silicate cement.\(^{18–20}\)

### 3. The mechanisms in chloride binding of cement-based material

No matter where the chloride ions causing the corrosion of cement-based materials are coming from, it has been generally recognized that the chloride ions exist in three main identified modality: the free chloride ions in pore solution, the physically bound chloride and the chemically bound chloride. Generally the physically bound chloride ions are inclined to be released, so part of physically bound chloride ions might convert into water-soluble chloride ions, especially when the temperature is elevated.\(^{15,24,70}\) Whereas compared with the physically bound chloride, the chloride ions bound chemically are much more immune to the variation of some environment both in internal and external.

Distinctly the various chloride binding mechanisms are affected by many factors in cementitious system, such as: the content of aluminates, Ca/Si ratio of C–S–H gel,\(^{53,64}\) the environment of pore solution and so on. Other than sulfate ions\(^{16}\) and hydroxide ions,\(^{67,68}\) furthermore metal cations\(^{28,29,45,72}\) has a crucial impact on the chloride binding capability in the development of hydration system in cement-based materials. Y. Yan\(^{23}\) resulted that for MK cement, the ability of chloride ions to solidify in different chloride salts fell into the following order: CaCl\(_2\) > MgCl\(_2\) > KCl > NaCl, in consequence the chloride ion curing rate of MK cement will reduce with the increasing pH value of the soaking solution. Indeed, when different chloride salts\(^{15,27,28,65}\) are dissolved into aqueous solution, the released cations, i.e. Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\), Na\(^{+}\), will induce the more OH\(^{-}\) compete with chloride ions for attaching into the ‘electric double layers’ with the varying pH.\(^{70,73}\) When it comes to the PH effect on the chloride binding capability, diverse anions should be reckoned with.

K. De Weerdt, A. Colombo et al.\(^{72}\) put forward that for the different associate cations, the effect of the chloride concentration of the exposure solution on the AFm and Aft phases are quite similar. When the specimens were exposed in distilled water, the AFm and Aft phases were supposed to form hemicarbonate and ettringite. Moreover, with the increasing chloride concentration, Kuzel’s salt and ettringite can be generated, which resulting from the decomposition of monosulphate. At even higher concentrations, the hemicarbonate and Kuzel’s salt can be replaced with Friedel’s salt, the sulphates formerly are bound in monosulphate, and Kuzel’s salt are bound in ettringite, as shown in Fig. 3.

M. Balonis et al.\(^{74}\) studied the impact of chloride on the mineralogy of hydrated Portland cement systems, they found that the varied rate of Cl\(^{-}\)/OH\(^{-}\) can lead to the change of the basal spacing of Friedel’s salt, likewise the alteration on the mineralogy of Friedel’s salt, which is described as Fig. 4.

In the past decades, there has been many researcher concentrated on the complex mechanisms of binding...
chloride ions in cement-based materials, but thus for some issues still remain to be dealt with, such as (1) the conditions for transformation between Kuzel’s salt (Ks) and Friedel’s salt (Fs); (2) the reasonable and authoritative methods for distinguishing the concentration of physically bound chloride ions from chloride ions bound chemically respectively hung in doubt. Those issues are directly related to the cognition in identifying the effects between physical and chemical chloride binding respectively, also are the hinge to the distinguish the quantity of free chloride ions from hydrolysoluble chloride ions. Finally, the section will generalize the relevant mechanisms both of physical chloride binding and chemical chloride binding by focusing on the micro-structure of cementitious materials with bound chloride ions and the corresponded chloride binding isotherms.73,83

3.1 The mechanisms of physical chloride binding

As presented in the section of 1.2, physically chloride binding is impacted by sundry factors, such as temperature, internal chemical environment (the component of pore solution and hydration products), likewise some external interactions,62,68,75 e.g. sulfate attack, other salts leaching, carbonation. Once the cementitious material is blended with the mixing water, the positive ions likewise Mg2+, Ca2+, K+, and Na+ are dissolved into the solution instantly as the process of hydration in the blender system, which gives rise to the negative charge of cement surface. K. De Weerdt and A. Colombo et al.73,72,86 believed that C–S–H gel could absorb cations, such as Ca2+, Mg2+, K+, and Na+, then the ions with negative charges [i.e. chloride ions (Cl−), hydroxide ions (OH−), nitrate ion (NO3−)] can be adsorbed by the newly formed electricity layer for the balance of electricity price.74,77 Moreover, the potential of the double layer subject to valence of the absorbed cation, especially, as well as the curing temperature is related to the concentration of chloride ions in the pore solution,24,29,68,70 which has a decisive influence on chloride binding capacity of cement-based materials. The theory of double electric layer (DEL)44,52,53 has been well accepted to illustrate the mechanism of physical chloride binding. DEL consists of two parts: fixed layer (a nonflowing layer that clinging to the surface of cementitious particles) and the flowable diffusion double layer on which the surplus of ions with opposite charges is gradually reducing to naught.78 The fixed layer containing the bound chloride ions and the surplus of other ions with foreign charges. The hydration product of the cementing material can selectively absorb some charged ions and some excess foreign ions to form a fixed layer with a total electric potential of Φ, and absorb another part of excess foreign ions in the diffusion layer with a electric potential of ζ, consequently a DEL form in the hydration product of concrete.

Chloride ion can promote the ions with opposite charges to enter the fixed layer of DEL in cementing concrete hydration product, so that the thickness and electric potential ζ of DEL are reduced. Meanwhile, in this process chloride ions are difficult to diffuse to the deep layer of concrete resulting from the repulsion by the electric charge of the double layer. Obviously, this repulsion mainly depends on the distance from chloride ions to the fixed layer. The shorter distance, the more chloride ions were repelled by the charges of the double layer lead to the more difficult it is to diffuse.24,77 When the chloride ion is out the range of the double layer, the electric potential of the double layer is zero, then the effect of the double layer on chloride ion diffusion is quite weak. There is a mutual repulsion between the two electric layers existing on the solid–liquid interface, based on which they will repel each other while two parallel electric layers are close to each other.

The physically chloride binding capability is mainly based on DEL in the system of cement-based materials. Chloride ions diffusing into concrete are bound to be squeezed into the fixed layer and/or diffusion layer,79 free chloride ions are stabilized because of the interaction of electric charge, forming a new DEL. On one hand, the new DEL has certain hindrance to the chloride diffusion. On the other, the DEL can physically bind chloride ions, so that the concentration of free chloride ions can be descended in
the pore solution and the service life of concrete can be extended. But charge attraction is relatively weak and vulnerable to variation of environment. With the extension of service life, increasing chloride ions diffused into concrete, while the amount of negative ions that can be squeezed into the fixed layer are limited, therefore the chloride binding capability in the double layer will become reducing. However, when the aperture structure of concrete is refined and the pore size distribution tends to be optimized, the physically chloride binding ability can keep lasting respectively. Under the action of the electric double layer, chloride ion can be physically adsorbed on the surface and the inner pores of C–S–H gel layer, but it also can be tightly solidified in the C–S–H microcrystalline lattice, as V. S. Ramachandran78) stated.

The micro-structure of C–S–H gel also exert vital effect on the physically chloride binding in cement-based materials. C–S–H gel can be classified into calcium silicate hydration with high alkalinity (C/S ≥ 1.5) and calcium silicate hydration with low alkalinity (C/S < 1.5) by the calcium-silicate ratio.24),31) The lower C/S means the smaller particles of crystal, the better mechanical strength, as well as the larger specific surface area with more contact points, these all due to degree of polymerization of silicon-oxygen chains. Moreover, in comparison to the calcium silicate hydrate with high alkalinity (C/S ≥ 1.5), calcium silicate hydrate with low alkalinity (C/S < 1.5) is superior in stability because of the extremely low solubility.33)

3.2 The mechanisms of chemical chloride binding

Once chlorine salts immersed in cement-based materials touch with cement clinker tricalcium aluminate (C₃A), tetra calcium aluminoferrite (C₄AF), then the chloride ions released from chlorine salts will react with various hydration products in the system of cement matrix materials, i.e., AFm, Aft, partially C₂AH₆. The reaction between chloride ions introduced in the form of NaCl and C₃A as example, the equation equilibria of adsorption precipitation reaction:16),52),55) $\text{CaCl}_2 + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 4\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ (1)

The reaction between chloride ions introduced in the form of NaCl and C₃A is as follows:

$2\text{NaCl} + \text{Ca(OH)}_2 \rightarrow \text{CaCl}_2 + 2\text{NaOH}$ (2)
$3\text{CaCl}_2 + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 4\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ (3)

3.2.2 Ion exchange mechanism

As ion exchange mechanism indicated that C₃A reacts with CaSO₄·2H₂O to generate ettringite in early stage hydration of cement, as shown in Eq. (4).10) With the consistent consumption of CaSO₄·2H₂O, the formed can react with the remanent C₃A to produce a single sulphate-type calcium sulphoaluminate, as formula (5):16),34)

$\text{C}_3\text{A} + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{C}_3\text{A}_2\text{SO}_4 \cdot 3\text{H}_2\text{O} \rightarrow 3\text{C}_3\text{A}_2\text{SO}_4 \cdot 3\text{H}_2\text{O} + 4\text{H}_2\text{O}$ (4)

$\text{C}_3\text{A} + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow 3\text{C}_3\text{A}_2\text{SO}_4 \cdot 3\text{H}_2\text{O} + 6\text{H}_2\text{O}$ (5)

In the ion exchange hypothesis, when $X^-$ (i.e., OH⁻, SO₄²⁻, CO₃²⁻ or NO₃⁻) is replaced with electronegative $X^-$, $[\text{Ca}_2(\text{Al})(\text{OH})_6] \cdot \text{X}^- \cdot n\text{H}_2\text{O}$ will convert to be Friedel’s salt, which well illustrate the process of the interaction between extraneous chloride ions and hydrated products of cement matrix. The relevant formula16),34) as follow:
\[ R\text{-OH} + Cl^- + Na^+ \rightarrow R\text{-Cl} + OH^- + Na^+ \] (6)

(Where R refers to AFm’s structure).

However, A. K. Surgavanshi et al.\textsuperscript{16} pointed out that when chloride ions were mixed into the cement-based materials, that only minor of which can substitute for the OH\(^-\) of the AFm-OH to transform AFm-Cl under the effect of ions exchange between chloride ions and hydroxy.

3.3 The correlation on the mechanisms both in physically chloride binding and chemically chloride binding

Based on the ion exchange mechanism, A. Delagrange, J. Marchand et al.\textsuperscript{80} also proposed the in process of conversation of AFm-OH into AFm-Cl, because the chloride ions of chloride salt substitute for the hydroxy ions of the AFm-OH, the positive ions of chloride salt dissolving into pore solution lead to excessive positive charges subject to the increasing concentration of positive ions.\textsuperscript{67,69} In order to the charge neutralization, the hydroxide (OH\(^-\)) in AFm-OH is released to pore solution, namely \([Cl^-]_{\text{bound}} = [OH^-]_{\text{released}}\). Whereas, for the adsorption precipitation mechanism, the positive ions of chloride salts dissolving into aqueous phase will be adsorbed by the C–S–H gel with large specific surface, meantime the C–S–H gel releases the equal quantity of protons into the pore solution\textsuperscript{81} suggested ion exchange mechanism and adsorption precipitation mechanism both attribute for chemically chloride binding simultaneously. Hence, in certain sense, there might exist in synergistic effect between chemically chloride binding and physically chloride binding. What’s more, some researches suggest that when specimens were long-term exposure to seawater that the major of the bound chloride ions still preferred to be chemically and/or physically bound by the C–S–H gel rather than being bound by observable crystalline chemicals.

There are two main model appropriate for exhibiting the correlation between bound chloride ions and free chloride ions, namely Langmuir model and Freundlich model\textsuperscript{12,16,44,49}.

Langmuir isothermal equation: 
\[ C_b = \frac{aC_f}{(1 + bC_f)} \]  
(7)

Freundlich isothermal equation: 
\[ C_b = \alpha C_f^\beta \]  
(8)

\(C_b\): the concentration of bound chloride ions; \(C_f\): the concentration of free chloride ions; the value of \(a, b, \alpha, \beta\) respectively depend on the characteristics of the hydration products involved in binding chloride ions. It has been well recognized that Freundlich’s isothermal equation is
compatible with the external chloride concentration which is higher than 0.01 mol/L.\(^{12,25}\) However, the Langmuir isothermal equation is applicable to low chloride ion concentration, namely, the chloride concentration is lower than 0.05 mol L\(^{-1}\).\(^{47,70,80}\)

4. The correlation between impermeability and chloride binding capability

Traditionally, the resistance to chloride erosion is characterized by resistance to chloride ions permeation which based on the results of a series of permeability test and chloride migration test.\(^{3,13,49}\) Numerical modelling results have showed that the capability of chloride binding can dramatically obstacle the chloride diffusion in concrete. Especially for prolonging exposure time, the chloride diffusion is expected to be impeded further considerably under the function of chloride binding. Indubitably, there are reasonable correlations among the chloride binding, anti-permeability and resistance to chloride corrosion, as abundant researches manifested. But until now, no one established standard regards chloride binding as a evaluation index of resistance to chloride erosion.\(^{70}\)

Whether for chloride diffusion or chloride migration, there are the same factors which exert different degrees of effect on those, those influential aspects also decide the chloride binding capability,\(^{43,51,54}\) such as water-binder ratio, curing conditions, supplementary cementitious materials and so on. Generally, higher curing temperature can trigger more quickly speed of reaction,\(^{28}\) such as the binding, migration and diffusion of chloride ions. Thereby the curing temperature has crucial influence on the amount of bound chloride ions, free chloride as well as the released chloride ions by hydrated products respectively. As O. R. Ogorirgo and L. Black\(^{26}\) illustrated that when slag replaced CEM I 52.5 R by 30 wt %, the temperature elevating from 20 to 38°C provided more attribution for chloride binding rather than chloride diffusion as well as chloride migration. Hence the resistance to chloride ions was upgraded as a whole.

As for cement-based materials, supplementary cementitious materials generally exert positive impact on chloride binding ability of cement-based materials, meanwhile supporting for the great resistance to chloride permeation might depend on the synergistic effect each other. But there’s no gainsaying that some mineral admixtures are in favor of the improvement of anti-permeability, while which are prejudicial to chloride binding capacity, such as silica fume\(^{31,55}\) and phosphorous slag.\(^{18-20}\)

With regard to chloride ions in the gas and liquid inside of the cement-based materials system, there are four kinds of permeable mechanism: chloride adsorption, capillary permeability (produced by the pressure gradient), chloride diffusion (produced by the concentration gradient) and migration (generated by the electric potential gradient).\(^{37,38,76}\) Thus it can be seen that the amount, distribution and morphology features of capillary pores was depended on the micro-structure. Capillary pores can provide channels for various charged ions\(^{20}\) (i.e. Cl\(^-\), OH\(^-\), K\(^+\), Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)), which can incur the variations both on the electric potential gradient and the concentration gradient. Furthermore, the chloride binding will alter as these variation and consequently make a difference on the impermeability to chloride ions in cement-matrix materials.

As D. K. Panesar et al.\(^{14,15}\) stated that the process of chloride binding can modify capillary pores by the effect of precipitate resulting from the formation of hydration products by chemically binding chloride ions. It needs to notice the attribution of chloride binding on the chloride anti-permeability. The numerous studies has resulted that the consistency of chloride binding capacity and chloride impermeability in cementitious composites with various mineral supplementary. The rank in contributions of mineral admixtures to chloride impermeability from high to low is phosphorous slag,\(^{20}\) MK,\(^{48}\) silica fume,\(^{49}\) BFS,\(^{24,67}\) FA\(^{12,56}\) and steel slag.\(^{35}\) Though phosphorous slag and silica fume are poor in chloride binding, but are excellent in chloride anti-permeability which due to their micro-aggregate filling effect and barrier effect,\(^{83}\) which trend to enhance the compactness instead of the reinforcing chloride binding with the chemical reactivity as well. Indeed, the chemically chloride binding capability mainly is depended on the chemical reactivity, while the physically chloride binding capability rests on the high specific surface area and high calcium to silicate ratio of hydrated products of cement-based materials.

5. The effect of chloride binding on service life prediction

Traditionally, there are numerous experimental methods on chloride diffusion and migration, which are employed to predict the service life of reinforced concrete in chlorinated environment.\(^{84}\) Whether for the non-steady-state or steady state diffusion-migration model, there have amount of researches which discovered that the chloride binding play a positive role on retarding the process of chloride transportation, namely chloride diffusion and migration. Definitely, for reinforced concrete attacked by chloride salts, there are three stages of the service life-span: initiation time (\(t_i = t_c\)), depassivation time (\(t_p\)), and corrosion (or propagation) time (\(t_{corr}\)).\(^{85}\) For chloride transportation, the impetus of chloride diffusion is the chloride concentration gradient, while chloride migration is promoted by electrical gradient.

Furthermore, there are several parameters corresponding to chloride diffusion-migration which applied for the prediction of service life of concrete constructions in chloride environment, as following: \(CTL\) (chloride threshold level), \(x\): the thickness of concrete cover, \(D\): the apparent diffusion coefficient, \(C_i\): the chloride concentration of concrete surface, which coincided with what H. W. Song, K. Y. Ann et al. Stated.\(^{86}\) These parameters are susceptible to chloride binding capacity, hence them make a remarkable sense for the prediction on service life of cementitious materials. Given the view of Fick’s first and second law or modified Fick’s second law, bound chloride ions have comprehensive influence on the time/depth dependency,\(^{84}\) the devel-
5.1 The effect of chloride binding on migration

Different with chloride diffusion, chloride migration is driven by the electrical gradient rather than concentration gradient. Apart from chloride diffusion, there are series of intricate interaction between chloride binding and chloride migration.

M. Maes, E. Gruyaert et al. calculated migration coefficients of concrete with BFS. They drew a conclusion that chloride binding behavior was in contrast with migration and diffusion coefficients, the resistance against chloride migration increased as BFS content increased, but the concrete with 70% BFS has the lowest binding capacity. In consequence, the effect of chloride binding on chloride migration is complex, and it is imperative for us to conduct more study on the issue in the future.

K. D. Stanish and J. Němeček et al. declared that internal electrical field can alter the properties of pore wall and reduce of the time free chloride ions contacting with binding site, which due to both the flux and accelerated movement of the various ion. It is supposed that the migration can lower the chloride binding velocity rather than the capability of chloride binding. The reason is that chloride binding sites exist constantly, although the time proper collisions occurring might be extended. It’s interesting to discover that during the rapid migration test, there are no chloride binding. The movement of chloride ions due to migration is subject to the equation:

$$\frac{\partial C}{\partial t} = D_{\text{mig}} \frac{\partial^2 C}{\partial x^2}$$  (9)

There is a relationship between the coefficient of migration: $D_{\text{mig}}$ and the diffusion coefficient: $D$, which can be expressed by the equation:

$$D_{\text{mig}} = \frac{zFE}{RT}D$$  (10)

This depicts the profile of the non-steady state, constant surface concentration situation is in similar form to Gran’s solution for diffusion:

$$C(x, t) = C_0 \text{erfc} \left( \frac{x}{2 \sqrt{D_{\text{mig}} t}} \right) = C_0 \text{erfc} \left( \frac{x}{2 \sqrt{D^*}} \right)$$

$$C_0 \left( 1 - \text{erf} \left( \frac{x}{2 \sqrt{D_{\text{mig}}}} \right) \right)$$  (11)

where: $C$ is the chloride concentration; $x$ is the depth of chloride permeation in concrete; $T$ is the temperature; $z$ is the valence of chloride; $F$ is Faraday’s Constant [9.648 × 10^4 J/(V·mol)]; $R$ is the universal gas constant [8.314 J/(mol·K)]; $C_0$ is the surface concentration; $t$ is the time; erf is the error function; erfc is the complementary error function; $D$ is the chloride diffusion coefficient; $E$ is the local electrical gradient.

5.2 The effect of chloride binding on the diffusion

On the premise of certain temperature, the relationship between the concentrations of bound chloridian and free chloridian can be represented by chloride binding isotherm. Based on the Fick’s second law, traditionally there are four theoretical curves used to characterize chloride binding isotherm as described below:

1) No binding

$$C_b = 0, \quad \frac{\partial C_b}{\partial C_i} = 0, \quad D^*_c = D_c$$  (12)

2) Linear binding

$$C_b = \alpha C_i, \quad \frac{\partial C_b}{\partial C_i} = \alpha, \quad D^*_c = \frac{D_c}{1 + \alpha/w_e}$$  (13)

$\alpha$ is the slope of the curve, it means the chloride binding rate value;

3) Langmuir binding

$$C_b = \frac{\alpha C_i}{1 + \beta C_i}, \quad \frac{\partial C_b}{\partial C_i} = \frac{\alpha}{(1 + \beta C_i)^2},$$

$$D^*_c = \frac{D_c}{1 + 1/w_e\alpha\beta C_i^{\beta-1}}$$  (14)

Where $\alpha$, $\beta$ are both of binding constants, which vary according to the concrete binder composition.

4) Freundlich binding

$$C_b = \alpha C_i^\beta, \quad \frac{\partial C_b}{\partial C_i} = \alpha \beta C_i^{\beta-1},$$

$$D^*_c = \frac{D_c}{1 + \alpha/w_e(1 + \beta C_i)}$$  (15)

where $\alpha$ and $\beta$ are the binding constants which vary basing on the concrete binder composition.

In these four mathematical model as above, where:

$C_b$ is the bound chloride concentration, kg/m³ of concrete; $C_i$ free chloride concentration, kg/m³ of concrete; $w_e$ is the unit evaporable water content in cement-based materials; $D_c$ is the effective diffusion coefficient, m²/s; $D^*_c$ is the apparent diffusion coefficient, m²/s; $x$: the depth of chloride penetration, mm; $t$: the time of chloride ingress, hours.

M. T. Liang, R. Huang et al. indicated that the following modified Fick’s second law equation with initial and boundary conditions [Eqs. (16)–(20)] as well as whose analytical solution [Eq. (21)], which can be expressed in terms of:

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left( D^*_c \cdot \frac{\partial C_i}{\partial x} \right)$$  (16)

$$C_i(x, 0) = 0$$  (17)

$$C_i(0, t) = C_s$$  (18)

$$C_i(L, t) = 0$$  (19)

with:
As the analytic solution for modified fick’s model, Eq. (21) uncovers the correlation among parameters: $D_c^*, C_f$, $x$, $t$. The left side of Eq. (21) is purely the area ratio between areas under the $D_c^*$-$C_f$ curve from $C_i$ to $C_f$ and $C_i$ to 0, respectively as shown in Fig. 7.\(^{90}\)

L. T. Liang, T. W. Yv et al.\(^{7,91}\) also researched the chlorination life prediction of reinforced concrete bridges by making use of four different models on chloride-binding isotherms (No binding; Linear binding; Langmuir binding; Freundlich binding). According to the results of investigation they concluded that: regardless of the constant or non-constant coefficient of diffusion, the free chloride concentration is more reasonable than total chloride as the index to evaluate the chlorination life of reinforced concrete. Moreover, when taking account of chloride binding for predicting the chlorination life of concrete, the rank based on percentage error of linear to nonlinear diffusion model, which is from small to large in the order as follow: Langmuir isotherm, linear binding, Freundlich isotherm and no binding. In fact, it’s the best approach to evaluate the service life of bridge deck in chloride environment to use Langmuir adsorption isotherm, meanwhile compared with other three model, the liner binding is the best for abutment and pier, as shown in Fig. 8.\(^{91}\)

5.3 The effect of chloride binding on the parametric values of corrosion in reinforced concrete

Given previous researching results on the effect chloride binding exerting on chloride transport, it is evident that chloride binding can make significant influence on the chlorination life for the concrete structures. Chloride diffusion should be mainly responsible for the chlorinated concrete due to chloride transportation, despite other incurring factors such as migration and absorption bring about the concrete corrosion.\(^{84,86}\) As well, Ulteriorly, there is correlation between the chloride migration and diffusion, which is accounted by Eq. (12). Therefore, undoubtedly it will
be simple and convenient for us to apply the parametric values underlying chloride diffusion to quantitatively analyse service life of concrete, which bases on the causticity and inhibition effect on concrete chlorination.

Submitted to the Fick’s second law and Fick’s law, generally there are four parametric values [expressed as Eq. (22)] deemed as the sensitivity analysis parameters to predict the life-span of serving cement-based materials, which is line with the study of H. W. Song and K. Y. Ann. Combined Eq. (22) with Fig. 5, we can realized that it supposed to be a reasonable and excellent method for the longer service life of reinforced concrete attacked by chloride salt to control the parameters in Eq. (22). For prolonging the service life-span of cement matrix materials, it’s meaningful to astrict the CTL as well as descend Cs and D by improving chloride binding capacity. Absolutely, it seems that larger concrete cover depth will be more effective for a loner corrosion-free life, however it’s almost impossible, which result from that the concrete cover depth must comply with the design and stipulations of engineering safety. In brief, it appears that the ideal approach is to control the D and Cs at a low level as possible, if a single aspect should be adopted. Otherwise, a combination of multiple measures can be taken for inhibiting of concrete corrosion in chlorination: likewise, boosting the CTL by 30%, as the same time, cutting down the D and Cs by 15% respectively.

\[
C(x, t) = C_s \left(1 - \text{erf} \frac{x}{\sqrt{2Dt}} \right)
\]  

(22)

Where: \(C(x, t)\) is the chloride concentration at the depth of concrete \(x\);
\(C_s\) is the superficial chloride concentration;
\(D\) equates the apparent diffusion coefficient;
\(t\) is the time.

Theoretically, we don’t know the value of \(D\), but it can be obtained according to \(C_s\) and \(C(x, t)\). The \(C_s\) and the \(D\) can predict the time for the CTL at the depth \(x\) of steel beyond the level triggering corrosion.

H. W. Song and K. Y. Ann manifested that \(x\) was the sensitive factor effecting on the corrosion-free life, CTL, \(C_s\) and \(D\) were along with the subsequent. The reference condition is identical for the modeled corrosion-free life as shown in Fig. 9 exhibited.

On the basis of embedded finite element formulation, N. Benkemoun, M. N. Hammood et al. established the model of chloride diffusion which considering with chloride binding in meso-scale concrete. They evaluated corrosion initiation time \(t_{corr}\) in function of different \(D\text{erf}/D\text{erf}\) either reflecting on chloride binding (“cb”) or non chloride binding (“ncb”) at various exposed time and the chloride binding capacity. They observed that, when taking account of chloride binding, the amount of free-chlorides (chlorides in solution) is marginal important to initiate chloride binding.
corrosion. With the effect of chloride binding, the results of their investigation stress that the corrosion initiation time $t_{\text{corr}}$ at any certain point can be longer. That’s because chloride binding can capture chloride from the diffusion flux, so as to retard the time span until corrosion initiation. All the results show that chloride binding capacity serve for the service life of concrete structures tremendously.

6. Summary and expectation

In brief, with respect to chloride binding capability, there are intricate influence factors as follow: different preparation technologies of multiple cement-based materials, different measurements on chloride binding capacity and the various erosion environment with diverse chlorine salts. All those resulted in the difficulties on comparisons of results. Thereby it is imperative for us to establish authoritative test procedures to quantify physical and chemical chloride binding capability of cement-based materials respectively in order to more exactly and rationally predict the service life of cementitious material in chlorine environment.

Moreover, for chloride binding capacity, it should be paid close attention on the influence of chemical additives on the interactions among multiple constituents of cement-based composites. Indeed, there’s lacking available information on the compatibility between chemical additives and mineral admixture in chloride binding capability. Therefore, it is expected to exploit appropriate chemical additives with positive impact on chloride binding to match cement matrix better.

Tricalcium aluminate ($C_3A$) and tetracalcium alumino-ferrite $C_4AF$ are conducive to chemically chloride binding by the formations of Friedel’s salt, Kuzel’s salt and other analogue hydrated products. Similarly, tricalcium silicate ($C_3S$) is the main force for physically chloride binding. Whereas high heat of hydration and fast setting time ascribe to $C_3A$ and $C_3S$ might cause a series of issues, which should be concerned about. Faced with those negative effects, the authors hold that compounding active mineral supplementary with the inert supplementary can adjust the pH of pore solution in certain range more than modest hydration heat and the work-ability of cementing materials. That might be a decent solution to hold great chloride binding capability with attention to favorable other performances of cementitious materials. For example, if phosphorus slag be compounded with high reactive mineral admixture, it might be on the promise of chloride binding ability in cement-based materials well.

Until now, there have been considerable researches concerning on chloride binding performance of cementitious paste and/or mortar, other than a few for available concrete specimens. The roles played by coarse aggregate and fine aggregate in chloride binding usually are neglected. However, it has been widely recognized that the sand ratio, grain size distribution, nominal diameter and other traits of aggregate are closely associated with the chloride corrosion. So it’s necessary for us to further consider the contribution of aggregate in chloride binding.

Generally, nanomaterials has many eminent qualities such as: huge specific surface area, excellent mechanical performance, and unique photoelectric performance and so on. Hence nanomaterials are broadly applied to multi-functional cement-based materials and the improvement of mechanical properties in cementitious materials. By contrast, it’s not widespread case that nanomaterials are applied to the development of durability in cement-based materials. There is more less instances about the application of nanomaterials to enhancing chloride binding ability of cement matrix. Actually, in theory the huge specific surface area of nanomaterials can provide more adsorption sites for chloride ions. Meantime some nanomaterials might have reactivity to accommodate the morphology, quality and distribution of hydration products in cement-matrix materials. Obviously, it makes momentous sense for broad application prospect of nanomaterials in chloride binding capability. Taking account of a series of complex influence of nano-materials making on cementing materials, there still are many works waiting us to deal with so as to tap outstanding potential of nanomaterials in improving chloride binding capability of cement-based materials.

Without doubts, chloride binding takes a positive part in chloride impermeability, but quantitative analysis is absent on the contribution of chloride binding capability to chloride anti-permeability. If associated models take account of the quantification on the contributions of chloride binding to chloride anti-permeability, it will be beneficial to drive further investigations on the resistance to chloride ion erosion.

Last but not least, based on electric-migration mechanism, electrical field is widely imposed to accelerate the desorption of bound chloride ions, which is similar with Rapid Chloride Permeability Test, Rapid Chloride Migration Test and NEL method. Nevertheless, there are some knotty problems to set reasonable electric experimental parameters, such as the charging time, electric voltage, electric current and so on. Those issues subject to the intricate interaction between electric field and cementitious material, especially when cement-based materials contain some conductive constituents. On the occasion, it’s in suspense that whether the chloride binding capability can be exactly evaluated. More important, it’s difficult to assure the results of measurements comply with the engineering practice, even the data of experiments is lack of application value.

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