



# Distance-associated chloride binding capacity of cement paste subjected to natural diffusion



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## HIGHLIGHTS

- Specimens undergoing natural diffusion are used for measuring the chloride binding capacity.
- Difference between conventional CBIs and natural-diffusion-determined CBIs is found.
- CBPs are proposed to quantify the hydroxyl-dependent chloride binding capacity.
- A hydroxyl-dependent chloride binding model is established.

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## ABSTRACT

Chloride binding capacity is usually quantified by chloride binding isotherms (CBIs). However, an important factor influencing chloride binding capacity, namely the internal chemical environment (ICE), cannot be represented in the conventional CBIs. Knowing the drawbacks of the conventional CBIs, this paper straightly put the emphasis on the distance-associated chloride binding capacity. Specimens undergoing natural diffusion were used for measuring the chloride binding capacity at different distance. CBIs, chloride binding profiles (CBPs), chemical profiles and microscopy result were performed to analyze the rules and mechanisms. From the results of CBIs and CBPs, it is found that the conventional laboratory-determined CBIs would overestimate the chloride binding capacity beyond a certain distance from the surface, and underestimate the chloride binding capacity near the surface. Based on the chemical profiles and the microscopy results, it is found that ICE changes greatly along with natural diffusion, and meanwhile the chloride binding capacity at different distance develops discriminatively with the ICE change. Plus, a hydroxyl-dependent chloride binding model is established to quantify the distance-associated chloride binding capacity. The model explains the difference between the conventional laboratory-determined CBIs and the natural-diffusion-determined CBIs, and it fits well with the test results.

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## 1. Introduction

Chloride-induced corrosion is one of the major causes of degradation of reinforced concrete structures [1–4]. It is known that a sufficient amount of chloride ions in concrete are able to break the passive layers ( $\gamma\text{-Fe}_2\text{O}_3$ ) of reinforcements, thereby substantially degrading the durability and service life of reinforced concrete structures [5]. According to the two-stage durability model [6], the induction stage, also known as the longest and the critical stage, is defined as a duration from the time chlorides firstly penetrated into concrete to the time a threshold level of chlorides reached the steel bar. At this stage, the penetrated

chlorides generally exist in two main forms in concrete, including free chlorides and bound chlorides. It is a widespread view that only free chlorides are immediately detrimental with regard to the reinforcement corrosion risk though some bound chlorides may be released at later ages [7–11]. As a result of binding, the time needed for free chlorides' reaching a threshold level has a considerable growth [12,13]. Knowing this, chloride binding capacity is commonly regarded as one of the most important factors deciding the length of service life of reinforced concrete structures.

Chloride binding includes physical binding and chemical binding. Neither of the two binding processes is a result of single reaction, but both contain various physical or chemical mechanisms [7,14]. Chemical binding in an early aged cement hydrate system mainly refers to the reaction between chlorides and unhydrated  $\text{C}_3\text{A}/\text{C}_4\text{AF}$  to form a Friedel's salt or its analogue [15,16]. In a mature

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cement hydrate system, however, chemical binding is possibly due to the anion exchange between chloride ions and AFm ( $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$ ) phases [17–19]. Actually, Friedel's salt or its analogue is also a specific kind of AFm phases. It is known that the AFm phases have a layered structure, which contains a positively charged octahedral principal layer  $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]^+$  and a negatively charged interlayer  $[\text{x.nH}_2\text{O}]^-$  [19,20]. In cement chemistry, the common species of the interlayer x anions are usually  $\text{Cl}^-$  (Friedel's salt),  $0.5\text{CO}_3^{2-}$  (Monocarboaluminate),  $\text{OH}^-$  (Hydroxy-AFm),  $0.5\text{SO}_4^{2-}$  (Monosulfoaluminate),  $0.5\text{Cl}^- + 0.25\text{SO}_4^{2-}$  (Kuzel's salt) etc. [21–24]. An AFm crystal may also contain more than one species of X anions to form solid solution [21]. The point is that the hydrogen bonds between principal layer and interlayer anions are weak and therefore the intruded chlorides can replace other species of interlayer anions of AFm phases to form Friedel's salt or analogue in the mature cement hydrated system [18]. Physical binding is neither unitary. Ramachandran pointed out three kinds of binding with C-S-H: in a chemisorbed layer on hydrated calcium silicates, present in the C-S-H interlayer spaces, and intimately bound in the C-S-H lattice [25].

It is because of the various binding mechanisms that chloride binding capacity is affected by many factors, e.g., content of aluminates, C/S ratio of C-S-H gel, sulfate ion concentration, hydroxyl ion concentration and cation type of pore solution [26–30]. In other words, chloride binding capacity is strongly impacted by internal chemical environment (abbreviated "ICE" below), which is known as the composition of pore solution and solid phases surrounding the location where chloride binding takes place. Likewise, some external interactions being able to influence the ICE could also impact the chloride binding, e.g. sulfate attack, leaching, carbonation [7,31,32]. Even in a normal chloride diffusion process, ICE would also gradually change, from the surface to the deep, along with chloride transport so as to keep electrical neutrality.

Chloride binding is often quantified at thermodynamic equilibrium by chloride binding isotherms (CBIs), which are known as the relationships between free and bound chloride ions over a range of chloride concentrations at a given temperature [8]. CBIs are usually provided with clear mathematical formulae and therefore they can be easily applied into the chloride transport models. Considering this, CBIs have attracted considerable attention from the researchers. Up to present, four types of binding isotherms (i.e., linear, Langmuir, Freundlich and BET binding isotherm) have been proposed to describe the chloride binding [33]. In order to determine suitable types and parameter values of CBIs, two main laboratory methods are frequently used in the existed studies [15,27,34]. According to the two methods, researchers need not to take samples from natural diffusion specimens but directly use powder or thin disc specimens, which are soaked in different concentrations of chloride solutions, instead. In that way, however, the chemical environment of chloride binding will not match the actual ICE of the concrete experiencing a natural diffusion. Likewise, the impact of the gradual ICE variation on chloride binding capacity cannot be precisely presented at different transport distance either. Therefore, it is perhaps not very proper to straightly use the conventional laboratory-determined CBIs to predict the chloride binding capacity at different distance of the concrete undergoing natural diffusion.

Knowing the drawbacks of the conventional laboratory-determined CBIs, this paper straightly put the emphasis on the distance-associated chloride binding in natural diffusion. A comparison between the conventional laboratory-determined CBIs and the natural-diffusion-determined CBIs is presented. A CBPs (Chloride binding profiles) method is also proposed to clearly analyze the chloride binding capacity at different distance of cement pastes undergoing chloride diffusion. The main purpose of this paper is to contribute to improving the understanding of distance-associated chloride binding capacity in a natural diffusion

process, and thereby promoting better evaluation of chloride binding capacity in practical engineering.

## 2. Materials and method

### 2.1. Materials

Ordinary Portland cement (OPC) was used and the detailed chemical composition of the cement is presented in Table 1. Neat cement pastes were prepared at water-to-cement (w/c) ratios of 0.30, 0.40, 0.50 and 0.60.

### 2.2. Specimens preparation and immersion test

6 cylindrical specimens (50 mm in diameter and 100 mm in height) and 30 disc specimens (50 mm in diameter and 3 mm in height) were casted for each w/c ratio. After curing in saturated limewater at  $20 \pm 1^\circ\text{C}$  for 28 days, the specimens were taken out for an immersion test.

The cylindrical specimens were used for measuring the chloride binding capacity at different distance after the immersion test. Prior to the immersion test, the cylindrical specimens underwent a surface treatment to implement the one-dimensional diffusion. In this work, the side and bottom surfaces of each specimen were sealed with epoxy resin, and only the top surface was kept unsealed. After that, the cylindrical specimens were exposed to a 0.5 mol/L NaCl solution for a period of 180 d. The solution tanks are covered with polythene sheets to avoid evaporations and carbonizations. In addition, the solutions were renewed every month for maintaining the chloride concentrations.

The disc specimens were used to determine the CBIs in a conventional way (taking no account of the distance). They were averagely divided into five groups and immersed in 0.1, 0.2, 0.3, 0.4 and 0.5 mol/L NaCl solutions, respectively. Considering that the thin discs are possibly easy to reach saturation, a much shorter immersion period, about one month, was set for these specimens. Polythene sheet covering was also used here to avoid evaporations and carbonizations.

### 2.3. Measurement of free chloride and other chemical concentrations

After immersion, the 6 cylindrical specimens were cut layer-by-layer from the exposed surface. The nominal thickness of each layer was 5 mm. The actual thickness of each layer, excluding the cut abrasion, is controlled within 3–4 mm. Before pressing, the specimen layers were converted to a saturated, surface-dry condition. Then each specimen layer was crushed into four or five small pieces. One or two pieces of each layer were randomly selected and temporarily stored for the following total chloride concentration measurement, and the rest pieces were used here for pressing the pore solution.

The small pieces from the same-distance layers of the six cylinders were stacked together and put into a presser. At a pressure up to 300 MPa, the pore solution was then slowly extracted out. When sufficient pore solution was obtained, it was divided into two parts and separately stored in two test-tubes. For one tube of solution, the free chloride concentration was measured using an automatic titrimeter. For the other, the chemical concentration of the pore solution was measured by flame photometry. Prior to titration, the PH value was also tested by a glass PH electrode in the first tube of solution.

The disposal of the 30 disc specimens was much easier because they need not be re-cut before pressing. After retaining samples for the total chloride concentration measurement, the crushed discs in the same group were straightly stacked in the presser to extract the pore solution. Later, the free chloride concentration, the PH value and the other chemical concentrations were measured using the above methods.

### 2.4. Measurement of total chloride concentrations

The restored specimen pieces were ground into powder using a mortar and pestle. Then an amount of powdered specimen was soaked in dilute nitric acid solution to determine the total chloride concentration. Each test result was given as an average of three replicates.

### 2.5. Microscopy test

A small flake sample was typically taken from the cylinder specimen with 0.5 w/c ratio. The flake was selected nearly parallel to the diffusion direction and perpendicular to the exposed surface. With the HITACHI S-3400N Scanning Electron Microscope (SEM), the micro morphology of the cement hydration was analyzed at different distances from the exposed surface. Besides, a linear Energy Dispersive X-ray Spectroscopy (EDS) scanning was also carried out in distance of 0–3 mm to analyze the chemical element profile in the surface region.

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