



Influence of cation type on diffusion behavior of chloride ions in concrete



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HIGHLIGHTS

- Chloride diffusion behavior associated with four common cations is studied.
- The model considering multi-phase reactions and ionic interactions is improved.
- The improved model is applicable for more common situations.
- Two important factors influencing the binding capacity are analyzed.

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ABSTRACT

In the previous paper, a model considering multi-phase reactions and ionic interactions was created to describe the diffusion behavior of chloride ions in concrete immersed in NaCl and CaCl₂ solutions. In this paper, more experimental tests and numerical simulations are conducted to improve the model and to study the influence of cation type on chloride diffusion behavior in concrete. In the experimental part, the total and the water-soluble chloride concentrations are determined after 180 days of immersion in the NaCl, KCl, MgCl₂ and CaCl₂ solutions. The test results show that the chloride binding capacities associated with the four cation types decrease in the order Ca²⁺ > Mg²⁺ > Na⁺ ≈ K⁺ while the apparent diffusion coefficients of them decrease in the order K⁺ ≈ Na⁺ > Ca²⁺ > Mg²⁺. In the numerical part, the equations of magnesium ions are newly considered so that the improved model can be applicable for more cation types. Based on the improved model, the chloride binding capacity of concrete in natural diffusion process is a complicated function concerning with many factors, among which the cation type and the contact duration are significantly important.

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1. Introduction

Chloride diffusion in concrete is the major cause of reinforcement corrosion which dominates the durability of reinforced concrete structures exposed to marine environments, salt lakes and de-icing salts [1]. Chloride diffusion in concrete is essentially a complicated physicochemical process that accompanies with ionic actions and multi-phase reactions. The existence of other ions in source or pore solutions would influence the diffusion behavior of chloride ions in concrete [2]. Even if only a single species of chloride salt is considered, the influence of the associated cation type still cannot be ignored.

K⁺, Na⁺, Ca²⁺ and Mg²⁺ are the four common cation types existed in marine environments and salt lakes. The detailed cation compositions of different environments are quite different. For example,

most of salt lakes are magnesium-rich while the groundwater in many areas is calcium-rich [3]. The chlorides associated with these cation types are also the common species of deicing salts which have been widely applied to control snow and ice on the road surface during winter [4]. Therefore, it is necessary to study the influence of cation type on the chloride diffusion behavior in concrete. Actually, many researchers have found the marked difference of the chloride diffusion behavior with different associated cation types. Chatterji et al. [5] have demonstrated that the diffusion coefficient, D , of Cl⁻ combined with divalent cation was greater than that combined with monovalent cation and decreased in the order $D_{Cl-(MgCl_2)} > D_{Cl-(CaCl_2)} > D_{Cl-(KCl)} > D_{Cl-(NaCl)}$. Arya et al. [6] have found that NaCl resulted in 43% bound chloride, far lower than CaCl₂ 65% and MgCl₂ 61%. Zhu et al. [7] have found the Chloride binding capacity with the associated cations decreased in the order Ca²⁺ > Mg²⁺ > Na⁺ ≈ K⁺. In the previous paper [8], two groups of tests were conducted to determine the concentration profiles of total and water-soluble chloride in

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concrete immersed in CaCl_2 and NaCl solutions. A model considering the multi-phase reactions and ionic interactions was also proposed to explain the marked difference between the two groups of test results. However, this model is not applicable for all the common cation types.

In this paper, the influence of K^+ , Na^+ , Ca^{2+} and Mg^{2+} on the diffusion behavior of chloride ions has been investigated. More numerical simulations are done to improve the previous model in order to describe the influence of the four cation types on the chloride diffusion behavior in concrete. This paper is aimed to enrich the experimental evidence and to thoroughly reveal the chloride diffusion behavior in concrete structures exposed to the chloride environments with the common cation types.

2. Materials and methods

2.1. Materials and concrete mix

In this investigation, type II Portland cement is used and the chemical compositions of the cement are given in Table 1. River sands with a fineness modulus of 2.8 are adopted as the fine aggregate. Gravels with a maximum size of 20 mm are utilized as the coarse aggregate. The mix proportion used in the experiments is given in Table 2.

2.2. Specimens preparation and immersion test

The concrete is casted into a slab of size 2000 mm * 2000 mm * 200 mm. After curing in saturated limewater at 20 ± 1 °C for 90 days, a group of cylinder specimens are drilled out from the slab and then cut into $\Phi 100$ mm * 50 mm. The side and bottom surfaces of the cylinder specimens are sealed with epoxy resin while the top surface is exposed to the source solutions for 6 months. The source solutions used in this paper are 0.5 mol/L NaCl_{aq} , 0.5 mol/L KCl_{aq} , 0.25 mol/L $\text{CaCl}_{2\text{aq}}$, and 0.25 mol/L $\text{MgCl}_{2\text{aq}}$, respectively.

2.3. Powder sampling and chloride titration

After immersion, the concrete specimens are milled to powder, layer by layer. The thickness of each layer is controlled within 1–3 mm. The powder which comes from the border area of each layer is discarded while the powder from the core area is passed through a powerful magnet to remove the ferrous powder which comes from the milling head. After that, the available powder of each layer is divided into two groups. One group is soaked in de-ionized water and the other one is soaked in dilute nitric acid solution to determine the water-soluble and total chloride concentration. The detailed procedures are the same as the methods used in the previous paper [8]. In the titration work, an automatic titrimeter is used to precisely determine the chloride concentrations.

2.4. XRD

By carefully removing the aggregates, paste in depth of 1–3 mm from the surface is taken to grind into powder which could go through 16 μm screen. Then the powder is dried at the temperature of 60 °C for 24 h for further XRD experiments. With the D8 ADVANCE X-ray powder diffractometer from RUKER AXS Company of German, the hydration products of cement-based material are analyzed. In the XRD test, Cu K α , 40 kV voltage, 30 mA current, scanning angle range from 5° to 80°, scanning speed of 10°/min and step length of 0.02° are used.

3. Results and discussion

3.1. Chloride profile

Fig. 1 shows the chloride concentration profiles of the specimens immersed in NaCl , KCl , MgCl_2 and CaCl_2 solutions for 6 months. The solid symbols present the total chloride concentrations while the hollow ones are the water soluble chloride concentrations (wt% of concrete). For each solution, the data of three

Table 2
Mixing proportions (kg/m^3).

w/c	Cement	Water	Sand	Gravel
0.50	312	156	746	1118

concrete specimens (CON1, CON2 and CON3) are given in the figure. It is found that the total chloride concentrations of the specimens immersed in CaCl_2 and MgCl_2 solutions are significantly larger than those of the specimens immersed in NaCl and KCl solutions while the water-soluble chloride concentrations of them are not so much different. This indicates the influence of cation type on the chloride diffusion behavior in concrete is mainly embodied in the different chloride binding capacity.

It is also found in Fig. 1 that the total chloride concentration profiles of NaCl , KCl and MgCl_2 solutions have an unexpected drop near the specimen surface. This kind of chloride drop has been frequently found in the concrete undergoing water dry/wet alternation, which is usually attributed to the effect of convection [8,9]. In this investigation, however, the chloride drop near the surface is probably not due to the convection effect since the concrete specimens are nearly water saturated after curing in limewater, as previously mentioned, for 90 days. A reasonable explanation is that the Ca^{2+} ions in the pore solution of concrete immersed in NaCl , KCl and MgCl_2 solutions would be leached out and the binding rate of chloride ions would be getting slower in the absence of Ca^{2+} owing to the Ca^{2+} ions are perhaps the most required accompanied cations in the chloride binding process especially in the chemical binding process.

3.2. Bound rate

The water-soluble concentrations were frequently used to estimate the free chloride since the good relationship between them though they are not thoroughly equal. Fig. 2 shows the bound rates calculated from the water-soluble concentrations. It is estimated that the max bound rates of CaCl_2 and MgCl_2 solutions are about 70%, which are much larger than 40% of NaCl and KCl solutions. The chloride binding capacities associated with different associated cations decrease in the order $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ \approx \text{K}^+$. This trend is similar to the previous workers' results [6,7].

It is noticed that the bound rates varies with the range of distance. The max or min bound rates is neither found in the surface nor in the deepest, which is different from all the existed binding isotherms. This indicates the bound rates are perhaps not a simple function of free chloride concentrations but influenced by many factors, such as cation type. Fig. 3 shows the relationships between the bound chloride concentrations and the water-soluble chloride concentrations. It is found that the binding rule in the natural diffusion test is different from the Freundlich or the Langmuir binding isotherm obtained in laboratory. Oppositely, it is more similar to the linear rule obtained in the field engineering by Mohammed and Sandberg [10,11]. Actually, the rule is not really linear, which would be discussed in the following part of simulations.

3.3. Apparent diffusion coefficient

The diffusion coefficients, which were calculated from the best fit of the Fick 2nd law to the total chloride profiles, are also given in

Table 1
Composition of cement (wt.%).

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO_2	P_2O_5
Content	21.70	5.09	4.32	64.64	0.92	1.08	0.21	0.53	0.14	0.10	0.05

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