- Technical paper -

# STUDY ON THE INFLUENCE OF VARIOUS INORGANIC SALTS ON ION TRANSPORT IN CEMENT-BASED MATERIAL

Worapatt RITTHICHAUY<sup>\*1</sup>, Takafumi SUGIYAMA<sup>\*2</sup> and Yukikazu TSUJI<sup>\*3</sup>

**ABSTRACT:** The influence of types of inorganic salt on diffusion of ions through mortar specimen made by different types of cement binder was experimentally investigated. The results showed that both the type of cement binder and the type of inorganic salt resulted in different diffusion behaviors. These different characteristics can be explained by transport properties of each coexisting ion and ion-solid interactions such as electrical double layer in a cement-based material. Furthermore, a pore structure coefficient that is defined using the effective diffusion coefficient from the steady-state migration test can be used to quantify the physical characteristic of mortar specimen.

**KEYWORDS:** ion transport, inorganic salt, membrane potential, electrical double layers, pore structure characteristic

## 1. INTRODUCTION

The influences of coexisting ions on the transport behavior of each ion in a multicomponent solution of the pore solution in a cement-based material such as mortar or concrete have been studied and modelled [1, 2]. Those analytical studies have shown that the movement of an ion with a particular charge will be effected by the other ions with both similar or opposite charge; hence the effect of coexisting ions is extremely important. Moreover, the developed calculation models have also shown that the influences of coexisting ions in the multicomponent solution have to be included for accurate prediction of the transport phenomena in a cement-based material especially in long term of service. However, the remarkable experimental evidences on the effect from the coexisting ions on ion transport in a cement-based material are rarely reported. In order to understand the effect of coexisting ions that results in different transport behaviors, various types of inorganic salt solution can be used to investigate these important phenomena.

The purpose of this experimental research is to investigate the effect of coexisting ions on the diffusion behaviors of each ion through mortar specimens made by different types of cement binder. The experimental program was the diffusion experiment of thin plate mortar specimen made by ordinary

Portland cement (hereafter OPC) and OPC mixed with lime powder (hereafter LP) 30% by weight of total binder. The solutions in upstream compartment were classified in three types of inorganic salt solution; sodium chloride (NaCl). potassium chloride (KCl), and calcium chloride (CaCl<sub>2</sub>) solutions with the concentration of the chloride ions of 0.5 mol/l while distilled water was used in downstream compartment.



Fig.1 Schematic diagram for ions transport calculation model in a cement-based material

\*1 Department of Civil Engineering, Gunma University, Graduate student, Member of JCI

<sup>\*2</sup> Department of Civil Engineering, Gunma University, Associate professor, Ph.D., Member of JCI

<sup>\*3</sup> Department of Civil Engineering, Gunma University, Professor, Dr.E., Member of JCI

In addition, the model for calculating the transport of ions in a cement-based material that is composed of the following three components as shown schematically in **Fig.1**; interaction between coexisting ions in a multicomponent solution [1, 2], pore structure characteristic which is evaluated by the steady-state migration experiment [2], and the ion-solid interaction phenomena which includes chemical reactions [2], membrane potential [3] and the existing charge on pore surface [4] is developed.

# 2. EXPERIMENTAL DETAILS

In the experimental programs for this study, the diffusion experiment of various types of inorganic salt and the steady-stage migration experiment by chloride ion were performed for the mortar specimens made by two types of the cement binder. The detail for each experiment will be explained in the following paragraphs.

## 2.1 PREPARATION OF MORTAR SPECIMEN

In present study, the experiments were performed by using the mortar specimen made by OPC and OPC mixed with LP (30% by weight of the total binder). The chemical compositions of OPC and LP are shown in **Table 1**. The mix proportions of mortar specimen and the physical properties are shown in **Table 2**. These mortar specimens were mixed by distilled water, cement binder and Toyoura standard sand (dry density: 2.62-2.64 g/cm<sup>3</sup>) without any additional chemical agent. The steel cylinder (10 cm diameter, 20 cm height) was used as the mold for mixed mortar. After 24 hours of mixing, the mortar was demolded and cured in a saturated Ca(OH)<sub>2</sub> solution for 3 months in the temperature-humidity controlled room (25°C, 60% RH.).

Table 1. Chemical composition of	f
cement binder (% of material)	

Compound	OPC	LP
CaO	64.3	-
CaCO <sub>3</sub>	-	98.7
SiO <sub>2</sub>	20.9	0.29
Al <sub>2</sub> O <sub>3</sub>	5.24	0.11
Fe <sub>2</sub> O <sub>3</sub>	2.88	0.09
SO <sub>3</sub>	2.05	0.03
Na <sub>2</sub> O	0.27	-
K <sub>2</sub> O	0.40	-

Table 2. Mix proportion of mortar specimen

Specimen	W/B (%)	S/B	Unit weight of material (kg/m <sup>3</sup> )				Slump flow	Compressive
			W	С	$C^*$	S	(mm)	strength (N/mm <sup>2</sup> )§
OPC	- 65	2.0	359	553	-	1106	225	37.3
LP		2.0	356	383	164	1094	240	21.5

C<sup>\*</sup>; Lime powder (30% by weight of total binder)

<sup>§</sup> 28 days compressive strength

## **2.2 DIFFUSION EXPERIMENT**

After the curing was completed for 3 months for each mix proportion, the cylindrical mortar was taken from the curing tank and then it was cut into a size of 100 mm diameter and 7 mm thickness. The circumferential surface of each slice was coated by the epoxy adhesive to ensure that there is only one direction of the ion diffusion. The coated specimen was placed to dry for 4 days in a condition of opened-air laboratory room, then the specimen was vacuumed under a saturated  $Ca(OH)_2$  solution for 24 hours before the diffusion experiment could be started.

The diffusion cell used in this experiment was shown schematically in Fig.2. In each experiment, 3 specimens were







 $Ca^{2+}$  diffused into downstream compartment was also measured by the atomic absorption spectrophotometer. However, in the similar elapse time, this value has to be deducted by the leaching amount of the same ion from the parallel test of leaching experiment (distilled water as leachant) which performed by the similar size and mix proportion of mortar specimen as shown in **Eq.1**.

$$Q_{i}^{t} = \sum_{t=1}^{\infty} \left( C_{i}^{t} V_{i}^{t} - C_{i*}^{t} V_{i*}^{t} \right)$$
(1)

where,  $Q_i^t$ : cumulative diffusive amount of ion i at time t (mg),  $C_i^t$ : measured concentration of ion i in the diffusion experiment at time t (mg/l),  $V_i^t$ : volume of the solution in the diffusion experiment at time t (l),  $C_{i^*}^t$ : measured concentration of ion i in the parallel leaching experiment at time t (mg/l),  $V_{i^*}^t$ : volume of the solution in the parallel leaching experiment at time t (l).

The renewing of the solution in both compartments was done in every two weeks. The experiment was completed after the steady-state of Cl<sup>-</sup> in downstream compartment could be achieved.

## **2.3 MIGRATION EXPERIMENT**

In parallel to the diffusion experiment, the steady-state migration experiment was also carried out for both types of mortar specimen. The cylindrical shape of 100 mm diameter and 50 mm thickness was cut after 3 months curing. The pre-conditionings of specimen in this experiment were similar to those in the diffusion experiment. In each experiment, 3 of specimens were also performed for each mix proportion. The migration cell used in this experiment was shown schematically in **Fig.3**. The upstream compartment was filled with 1 liter of 0.5 mol/l NaCl solution, while that in downstream compartment was



Fig.3 Migration experiment apparatus

1 liter of 0.3 mol/l NaOH solution. The measurement of Cl<sup>-</sup> concentration was carried out in both upstream and downstream compartments by AgCl auto-titration apparatus. The experiment was completed after the steady-state of Cl<sup>-</sup> in downstream compartment could be achieved.

# **3** ESTABLISHMENT OF THE TRANSPORT CALCULATION MODEL

As mentioned in the former part, the calculation model for transport of ions in a cement-based material was developed in present study. This calculation model is composed of three components as shown schematically in **Fig.1**. These three components are the interaction between ions that coexisting in the multicomponent solution, the pore structure characteristic of a cement-based material, and the ion-solid interactions or the chemical equilibriums occurred during the transport of ion through the pore solution of hydrated material. Therefore, these phenomena or activities have to be included for calculation of ion transport in a cement-based material as explained in the following paragraphs.

#### **3.1 INTERACTION FROM COEXISTING IONS**

The transport model presented in this study has been developed in the previous work [1, 2]. The interaction from the coexisting ions in the multicomponent solution system is considered as the mutual diffusion coefficient shown in **Eq.2**. This mutual diffusion coefficient,  $D_{ij}$ , contributes to the diffusion coefficient of ion species  $i_{th}$  that influenced by the concentration gradient from ion species  $j_{th}$ .

$$\mathbf{D}_{ij} = \delta_{ij} \mathbf{D}_{i}^{0} \left(1 + \frac{\partial \ln \gamma_{i}}{\partial \ln C_{i}}\right) - \left\{ \frac{z_{i} \mathbf{D}_{i}^{0} C_{i}}{\sum_{k=1}^{n_{s}} z_{k}^{2} \mathbf{D}_{k}^{0} C_{k}} z_{j} \mathbf{D}_{j}^{0} \left(1 + \frac{\partial \ln \gamma_{j}}{\partial \ln C_{j}}\right) \right\}$$
(2)

#### **3.2 PORE STRUCTURE CHARACTERISTIC**

The pore structure characteristic of a cement-based material was experimentally investigated in this study [2]. The pore structure coefficient (K) is related to the intrinsic mutual diffusion coefficient ( $D_{ij,I}$ ) as shown in **Eq.3**. This coefficient is considered to reflect to the pore structure characteristic of a

cement-based material such as porosity, tortuosity, and the constrictivity as shown in the relation of **Eq.4**. In this study, this value is evaluated by using the effective diffusion coefficient ( $D_e$ ) of Cl<sup>-</sup> from the steady-state migration experiment and used for the present calculation model as shown in **Eq.5** [2].

$$\mathbf{D}_{ij,I} = \mathbf{D}_{ij}\mathbf{K} \tag{3}$$

$$K = \delta \frac{\varepsilon(x,t)}{\tau^2(x,t)}$$
(4)

$$D_{e} = D_{f} \left( \delta \frac{\varepsilon(x,t)}{\tau^{2}(x,t)} \right)$$
(5)

where,  $D_e$ : the effective diffusion coefficient from steady-state migration experiment (m<sup>2</sup>/s),  $D_f$ : the diffusion coefficient of trace ion as the Cl<sup>-</sup> in free solution (m<sup>2</sup>/s),  $\epsilon(x,t)$ : the porosity,  $\tau(x,t)$ : the tortuosity, and  $\delta$ : the constrictivity of the pore structure which is assumed to be 1.0 for this study. However, the constrictivity,  $\delta$  would be evaluated by the ion-solid interaction explained below.

#### **3.3 ION-SOLID INTERACTIONS**

In present study, the ion-solid interactions or chemical equilibriums occurred in a cement-based material during the transport of ions are also included in the calculation model as explained in the following paragraphs.

(1) Solid calcium leaching and chloride binding

The leaching mechanism of solid calcium  $(Ca(OH)_2 \text{ and } C-S-H)$  from the solid structure of a cement-based material and the chemical equilibrium for chloride binding isotherm are implemented in this calculation model as explained in the previous work [2].

(2) Membrane potential ( $\Phi$ )

The membrane potential is believed to exist when there is the difference between the concentrations of ions composition across the membrane. Zhang and Buenfeld [3] had studied the significance of the membrane potential existed from diffusion experiment by using different inorganic salt solutions. The membrane potential for OPC was evaluated to be -60 mV/cm according to the results of their study, although it may be theoretically calculated with the Goldman's Equation. Therefore, this effect has been implemented in the present calculation model as shown in the right part of Eq.6.

$$\frac{\partial C_{i}}{\partial t} = \sum_{i=1}^{n_{s}} D_{ij,1} \frac{\partial^{2} C_{j}}{\partial x^{2}} + D_{ii,1} \frac{FZ_{i}}{RT} \frac{\partial C_{i}}{\partial x} \frac{\partial \Phi}{\partial x}$$
(6)

(3) Pore surface charge

The negative charge on the surface of the pore structure of a cement-based material in the form of zeta potential. The charge amount is calculated based on the assumption proposed by Chatterji and Kawamura [4]. This effect can be considered that it influences on the transport of ions in the mechanism of disturbance to the electro-neutrality constraint of the pore solution. Therefore, the effect of surplus amount of the charge on the pore surface in the pore solution system is also included in the present study.

## 4. RESULTS AND DISCUSSIONS

#### **4.1 EXPERIMENTAL RESULTS**

The effective diffusion coefficients  $(D_e^{M}_{Cl})$  from migration test shown in **Table 3** will be used for calculation of pore structure coefficient of each specimen. The diffusion coefficients from diffusion test  $(D^D)$  calculated by Fick's 1<sup>st</sup> law of each ion are also shown in the same table for Cl<sup>-</sup> and cations. Because the concentration of Ca<sup>2+</sup> used in salt solution is lower than those of other cations, and it shows lower tracer diffusion coefficient in dilute solution than the other ions, therefore, it is

Table 3. Diffusion coefficient of each ion (×10<sup>-7</sup>cm<sup>2</sup>/s)

Specimen	D <sub>e</sub> <sup>M</sup> <sub>Cl-</sub>	$D^{D}$	NaCl	KCl	CaCl <sub>2</sub>
OPC	1.38	D <sup>D</sup> <sub>Cl-</sub>	1.24	1.49	1.07
		$D^{D}_{+}$	0.32	0.67	
LP	1.93	D <sup>D</sup> <sub>Cl-</sub>	1.48	1.99	1.40
		$D^{D_+}$	0.46	1.24	

\* Average for 3 specimens

considered to result in the undetectable amount of diffused  $Ca^{2+}$  from upstream compartment. In the calculation of  $D^{D}$ , it was assumed that the concentration gradient exists due to the difference between the concentration of ions in upstream compartment and that in downstream compartment not the concentration inside the specimen as shown in **Fig.4**.



Fig. 4 Assumed concentration difference in diffusion cell

#### 4.2 COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS





From the results shown in Fig.5, it is cleared that the model allows calculating the amount of diffusive ion from the upstream compartment where the effect of existing ion in the pore solution is also included. From the beginning of experiment. the diffusive amounts of ion can be noticed due to the leaching from the ion initially presents in the pore solution contacted with distilled water as shown by dotted line in Fig.5(a) and Fig.5(b). Therefore, ion in the triangle area can be considered to be the ion from upstream compartments. The domination time of ion from upstream compartment is justified by the time that cumulative amount of ion leaching from pore solution Those are is almost constant. around 20 days for both two ions. The results from leaching of solid calcium from specimen can also be calculated as shown in Fig.5(c) which shows good agreement to the experimental results.

The experimental results are influenced by various factors such as environment or the phenomena in micro-structure of the specimen itself. Therefore, scatters can be



Fig.6 Results of OPC specimens Fig.7 Results of LP specimens

observed in some specimens. By comparison between **Fig.5(b)** and **Fig.5(c)**, even though the amount of  $Ca^{2+}$  from calcium leaching should result in higher amount than that of K<sup>+</sup>, due to the K<sup>+</sup> supplied from upstream compartment, K<sup>+</sup> shows higher diffusive amounts in both calculation and experimental results.

**Fig.6** and **Fig.7** show the diffusive amounts of Cl<sup>-</sup> with elapse time in downstream compartment for OPC specimens and LP specimens, respectively. From all figures, although the concentration of Cl<sup>-</sup> is identical in upstream compartment, the average flux of Cl<sup>-</sup> exhibits highest in case of KCl and lowest in case of CaCl<sub>2</sub>. This is also understood from the calculated diffusion coefficients shown in **Table 3**. In this table, the diffusion coefficients of Cl<sup>-</sup> for both specimen are in the order of  $D_{Cl}^{KCl}>D_{Cl}^{NaCl}>D_{Cl}^{CaCl2}$  which is similar to the fact found by Goto and Daimon [5]. This tendency is similar to the magnitude of the tracer diffusion coefficient of each cation that is also in the order of K<sup>+</sup>>Na<sup>+</sup>>Ca<sup>2+</sup>. Therefore, each cation differently influences to the transport of Cl<sup>-</sup> due to its mobility as the higher attraction force is resulted from higher tracer diffusion coefficient. The comparison between the fluxes of Cl<sup>-</sup> of OPC specimens and those of LP specimens shows that the fluxes of LP exhibited higher than that of OPC for every series. Therefore, the permeability of LP specimens was larger than that of OPC specimens.

From the comparison of **Fig.5** and **Fig.6**, it is remarkable that the diffusive fluxes of  $K^+$  and  $Na^+$  are lower than those of Cl<sup>-</sup> for OPC specimens. The reason of this fact can be explained partially by the theory of electrical double layer [4] as shown schematically in **Fig.8**. It is known that negatively charged pore surface results to this electrical double layer. The negative charge of pore surface will selectively attract the cations that results to lower diffusive amount compared to that of Cl<sup>-</sup>. Moreover, the effect of counting diffusion of OH<sup>-</sup> that may pronounce to the higher diffusion of Cl<sup>-</sup> can also be considered in this situation [6].



Fig.8 Diagram for electrical double layer

# 5. CONCLUSIONS

From the experimental investigation and the calculation model developed and explained in this study, the following conclusions can be drawn:

- 1. Depending on the types of inorganic salt solution, the different diffusive fluxes of chloride ions can be noticed from diffusion experiment. The different tracer diffusion coefficients of cations in the salt compound are considered to influence the transport of chloride ions through the mortar specimen.
- 2. The diffusion coefficient of K<sup>+</sup> becomes larger than that of Na<sup>+</sup>.
- 3. The pore structure coefficient evaluated from steady-state chloride migration experiment can be applied in the calculation model of ions transport in a cement-based material.
- 4. The ions transport model should include; ions-ions interaction, ions-solid interaction and the pore structure characteristic to consider most related phenomena of ions transport in a cement-based material.

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