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Evaluation of mineral admixtures on the viewpoint of chloride ion migration through mortar ☆

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Abstract

Recently, it has been said that deterioration of concrete structures occurs due to migration of ions, such as Cl^- or Na^+, through concrete. In addition, some electrochemical methods which control migration properties through concrete, like desalination or re-alkalization, are becoming more important. However, the mechanisms of ion migration, in electric fields, through concrete are not well understood. Moreover, the effects of mineral admixtures, such as fly ash, silica fume and ground-granulated blast furnace slag on ion migration through concrete have not been closely investigated. From this viewpoint, for the evaluation of mineral admixtures, the properties of chloride ion migration through mortar containing fly ash, silica fume and ground-granulated blast furnace slag have been investigated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Migration; Chloride ion; Nernst–Plank equation; Mobility; Transport number; Ground-granulated blast furnace slag; Silica fume; Fly ash

1. Introduction

For improved construction in the next millennium, durability of concrete is very important. In this situation, ion movement through concrete has to be evaluated more clearly and reasonably from the viewpoint of sustainable growth of the world. Therefore, chloride ion migration through concrete, forced by electric current, becomes an important movement for maintenance of concrete or concrete structures from the viewpoint of application of desalination or re-alkalization for deteriorated concrete structures [1–5].

Additionally, in these years, the relation between electro-chemical migration and diffusion coefficient of Cl^- ion through concrete has been more and more closely discussed in the world [6,7].

However, there is limited information on the ion migration properties through concrete. Especially, effects of mineral admixtures, such as fly ash, silica fume and ground-granulated blast furnace slag, on chloride ion migration are not clear. With this background, the authors tried to evaluate the properties of chloride ion migration through mortars containing mineral admixtures.

2. Test procedures

2.1. Materials

For making mortar specimens, normal portland cement was used. Its physical properties and chemical analysis are given in Table 1. As fine aggregate, Japanese local natural sand was prepared. F.M., specific gravity and absorption capacity of fine aggregate were 2.71, 2.61 and 1.78% respectively. As mineral admixtures, Japanese domestic fly ash (FA), ground-granulated blast furnace slag (BFS) and powder type silica fume imported from Norway (SF) were used. Their physical properties and main chemical composition are given in Table 1.

2.2. Mix proportions and curing condition

The proportions of the mortar are summarized in Table 2. The $\emptyset 100 \times 200\ mm^2$ cylindrical formworks

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Table 1
Physical properties and main chemical compositions of cement and mineral admixtures

	Unit	OPC	FA	BFS	SF
Physical properties					
Specific gravity		3.17	2.18	2.91	2.16
Fineness (Blaine)	cm^2/g	3270	3240	8070	–
(BET)	m^2/g	–	–	–	20.2
Moisture content	%	–	0.13	–	0.62
Chemical composition					
L.O.I	%	0.6	1.74	0.4	3.64
SiO_2	%	21.3	50.71	33.7	92.69
Al_2O_3	%	5.3	24.12	13.4	0.62
CaO	%	64.4	10.01	41.9	0.28
MgO	%	2.2	2.20	7.1	0.67
SO_3	%	1.9	0.38	–	0.04
Na_2O	%	0.2	2.12	0.2	0.28
K_2O	%	0.60	1.25	0.3	0.80

Table 2
Mix proportions of mortars

No.	Mineral admixture	Replacement ratio (%)[a]	*W/B*	*S/C*
1	None	–	0.3	2.5
2	None	–	0.5	0.3–2.5
3	None	–	0.7	2.5
4	Fly ash	30	0.3	2.5
5	Fly ash	30	0.5	2.5
6	Fly ash	40	0.5	2.5
7	Fly ash	30	0.7	2.5
8	Ground-granulated blast furnace slag	50	0.3	2.5
9	Ground-granulated blast furnace slag	50	0.5	2.5
10	Ground-granulated blast furnace slag	50	0.7	2.5
11	Ground-granulated blast furnace slag	40	0.5	2.5
12	Ground-granulated blast furnace slag	70	0.5	2.5
13	Silica fume	10	0.3	2.5
14	Silica fume	10	0.5	2.5
15	Silica fume	40	0.5	2.5
16	Silica fume	10	0.7	2.5

[a] Replacement ratio by weight (%).

were prepared for casting mortar. After casting, test specimens were cured for 28 days in an air-conditioned room at a constant temperature (20 ± 2°C) and humidity (more than 90% R.H.). Cured specimens were cut to the size of $\emptyset 100 \times 10$ mm^2 disks for the cell experiments.

3. Evaluation of ion migration through concrete

3.1. Outline of cell experiment

For the purpose of the evaluation of properties of ion migration through concrete, a migration cell, as shown in Fig. 1, was used. $NaCl^-$-5% water solution was used for the cathode side in the cell experiment. $Ca(OH)_2$ saturated solution was prepared as anode side cell solution. This solution was to prevent chlorine gas occurrence due to the decrease of pH. Titanium mesh was used as electrode. Direct electric current was constantly charged with 1.0 A/m^2 during testing. The constant charge of 1.0 A/m^2 gives about 2–3 V/cm of potential slopes to specimens. And such rebel of potential slope did not change solutions to be high temperature.

During the migration test, ion concentration changes as shown in Fig. 2. In this case, ΔQ_i (mol/l/s) shows ionic permeation velocity in steady state. Flux J_i (mol/cm^2/s) has the following relations with permeation velocity ΔQ_i. Therefore, ionic flux J_i can be calculated as follows:

$$J_i = Q_i \cdot \frac{V_{cell}}{A}, \qquad (1)$$

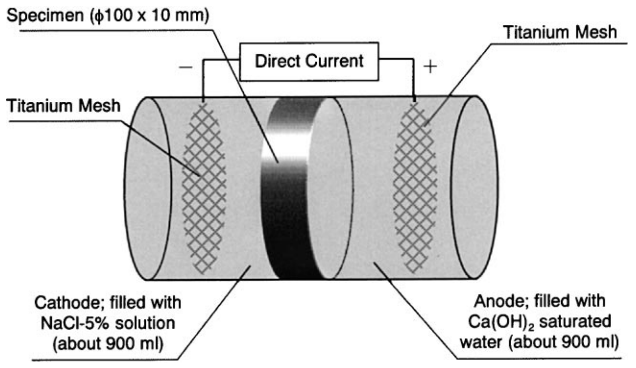

Fig. 1. Migration cell.

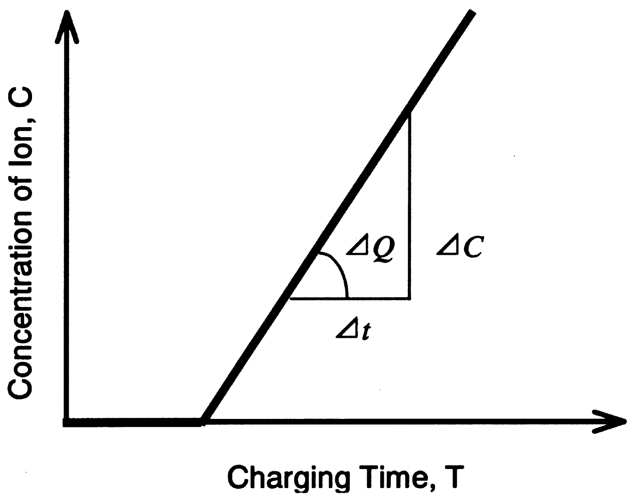

Fig. 2. Example of ionic flux during electric charging.

where V_{cell} is the amount of solution in anode side cell and A is the exposed surface area of the specimen (∅ 100 mm).

3.2. Physical significance of mobility and transport number as parameters of ionic migration through concrete

In Refs. [8–10], the authors clarified that when concrete is put into the electric field, almost all electric currents are moved only by the ion which exists in pore solutions in concrete. And this result could be considered that because of the very high electric resistance, compared to the bulk matrix of cement paste in concrete, electric current did not pass through the fine and course aggregate. In addition, the author gives the result that:

1. When the transportation number of chloride ion is small, electric current transports by another ion, such as Na^+, K^+, OH^-. This probably occurs when pore solution in concrete contains large amount of ions.
2. When the transportation number of chloride ion is large, electric current transports rather by chloride ion than Na^+, K^+, OH^-. This probably occurs when pore solution in concrete contains small amount of ions.

And these considerations can be supported by the famous Deby–Hückel theory. On the other hand, the mobility of ion means "the easiness of ion movement through porous media (of course including concrete)". From these considerations, the physical significance of mobility and transport number as parameters of ionic migration through concrete can be determined that:

1. Mobility shows the quality parameter of chloride ion movement.
2. Transport number shows the quantity parameter of chloride ion movement.

3.3. Calculation of ionic mobility by using the Nernst–Plank equation

The Nernst–Plank equation is a general equation for the ionic movement in water solution. The Nernst–Plank equation is shown as follows [11]:

$$J_{\mathrm{i}} = -D_{\mathrm{i}} \cdot \frac{\mathrm{d}C_{\mathrm{i}}}{\mathrm{d}x} - u_{\mathrm{i}} \cdot C_{\mathrm{i}} \cdot \frac{\mathrm{d}\phi}{\mathrm{d}x}, \qquad (2)$$

where D_{i} is the diffusion coefficient, C_{i} the ion concentration, u_{i} the electric mobility and $\mathrm{d}\phi/\mathrm{d}x$ is the electric potential.

The first term shows Fick's law in this equation. The second term means electric migration due to the electric potential. In the electric migration process, since the second term significantly increases, the first term of diffusion can be almost neglected. So, the ionic mobility u_{i} can be calculated as follows:

$$J_{\mathrm{i}} = -u_{\mathrm{i}} \cdot C_{\mathrm{i}} \cdot \frac{\mathrm{d}\phi}{\mathrm{d}x}$$

$$\text{therefore } u_{\mathrm{i}} = -\frac{J_{\mathrm{i}}}{C_{\mathrm{i}}} \cdot \frac{1}{\mathrm{d}\phi/\mathrm{d}x}, \qquad (3)$$

where, $\mathrm{d}\phi/\mathrm{d}x$ is the electric potential slope.

3.4. Calculation of ionic transport number

When the electric current density of 1.0 A/m^2 is charged between the electrode of the electrolytic cell, this means that 1 coulomb (C) passes in 1 s toward 1 m^2. The electric charge due to Cl^- in all the electric charges (the amount of total coulombs) becomes the ratio of the Cl^- in the amount of all the electricity movement. This is named as the transport number T of Cl^- (unit: none), that can be calculated by the following equation [8–11]:

$$T_{\mathrm{Cl}^-} = \frac{Q}{t_0}, \qquad (4)$$

$$t_0 = \frac{M \cdot I \cdot t}{z \cdot F}, \qquad (5)$$

where Q is the amount of chloride ion (g), t_0 the amount of chloride ion (g) in the case that all the movements of electric charge were due to the Cl^-, M the atomic weight (Cl = 35.5), $I \cdot t$ the amount of passed electric charge (C), z the ionic charge number (Cl = 1) and F is the Faraday's constant (96 500 C/mol).

4. Migration of chloride ion through mortar containing mineral admixtures

4.1. Relation between mineral admixtures and mobility

Mobility of Cl^- through hardened mortar with each mineral admixture is shown in Fig. 3. In this figure, mobility of the Cl^- through mortar changes remarkably by using mineral admixtures. Especially, when silica fume or ground-granulated blast furnace slag is used, even with water to binder ratio of 0.5 or 0.7, mobility of Cl^- is almost the same as that of $W/B = 0.3$ with no admixture.

The influence of replacement ratio of mineral admixtures on mobility of Cl^- through mortar with $W/B = 0.5$ and $S/C = 2.5$ is shown in Fig. 4. From this result, it can be considered that when silica fume or the ground-granulated blast furnace slag (8000 cm^2/g class) is used, mobility of Cl^- through mortar decreases. When silica fume is used, the decreasing tendency of Cl^- mobility is changed more than 10% of replacement ratio. As for the ground-granulated blast furnace slag (8000 cm^2/g class), the decreasing tendency of Cl^- mobility changes at about the replacement ratio of more than 40%. From these results, it was found that migration resistance against Cl^- can be improved remarkably by using silica fume or ground-granulated blast furnace slag.

It has been pointed out that the interfacial transition zone formed by aggregate-paste interface has large influence on the ionic movement through concrete. Therefore, these results can be considered that not only bulk paste but also the interfacial transition zone in hardened matrix becomes dense when silica fume or ground-granulated blast furnace slag are used.

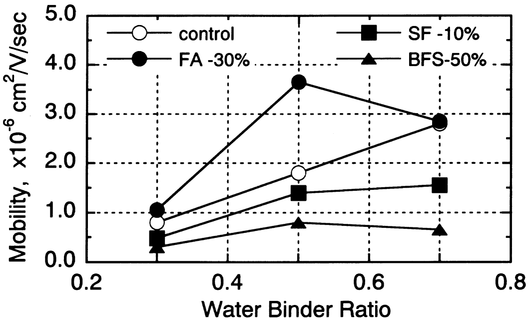

Fig. 3. Influence of water binder ratio on mobility of Cl^-.

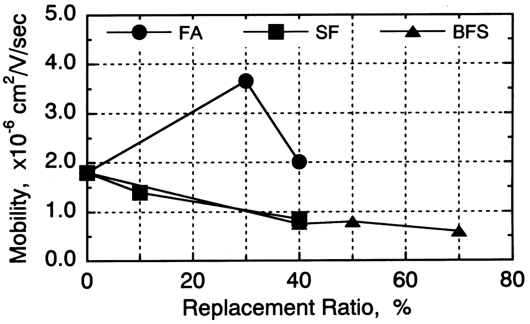

Fig. 4. Influence of replacement ratio on mobility of Cl^-.

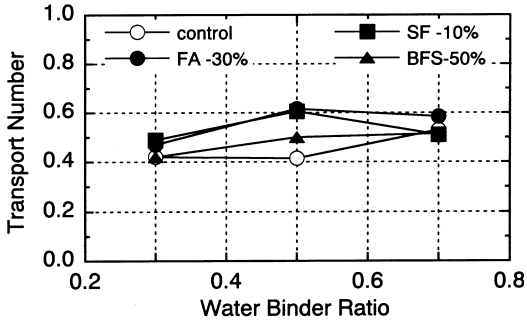

Fig. 5. Influence of water binder ratio on transport number of Cl^-.

4.2. Relation between mineral admixtures and transport number

The effect of mineral admixtures on transport number of Cl^- through mortar is shown in Fig. 5. The transport number of the Cl^- through mortar, for various replacement ratios of mineral admixtures is shown in Fig. 6. In these figures, the transport number of Cl^- is mostly in the range of 0.4–0.6 even when mineral admixtures are used. And, it can be noted that the transport number of Cl^- slightly increased when silica fume or fly ash was used. However, the relations between the transport number of Cl^- and mineral admixture are not so clear. Detailed further investigation is necessary about this point.

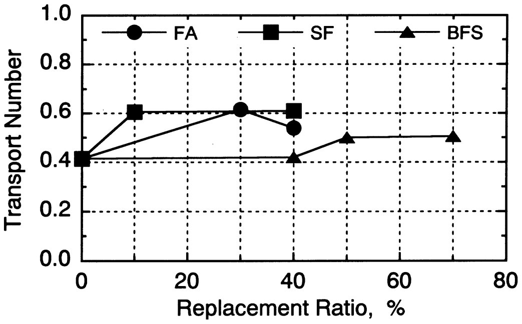

Fig. 6. Influence of replacement ratio on transport number of Cl^-.

5. Relation between materials and migration of chloride ion

Fig. 7 shows relation between the amount of unit binder in hardened mortar and mobility of Cl^-. It is clear from this figure that when mineral admixture is not used, mobility of Cl^- decreases caused by the increase of unit binder. On the other hand, as for the mortar specimen containing mineral admixtures, the tendency is different from the case of no admixtures. In addition, mobility of Cl^- with the amount of unit binder of 600 kg/m^3 which contains silica fume or ground-granulated blast furnace slag is almost equal to the mobility of mortar with the unit binder of 1000 kg/m^3 with no mineral admixtures. From these results, the migration properties of Cl^- through mortar might change greatly by the existence of mineral admixture. Especially, these change are more remarkable when ground-granulated blast furnace slag or silica fume are used.

Relations between Cl^- concentrations remained in mortars of each mix proportion after charging and mobility are shown in Fig. 8. The remaining concentration of Cl^- was measured by using crushed and granulated specimens after charging [12,13]. From this figure, the existence of mineral admixture and the kind of mineral admixture influence on mobility and concentration of Cl^- in mortars can be recognized. Silica fume and fly ash show the same tendency. However, in the case of ground-granulated blast furnace slag, there shows the different tendency compared to the cases of silica fume and fly ash. It can be considered that silica fume or fly ash has pozzolanic reactivity. On the other hand, ground-granulated blast furnace slag has different reactivity from silica fume and fly ash. Therefore, different forms of the hydration product in mortar might be produced in each cases.

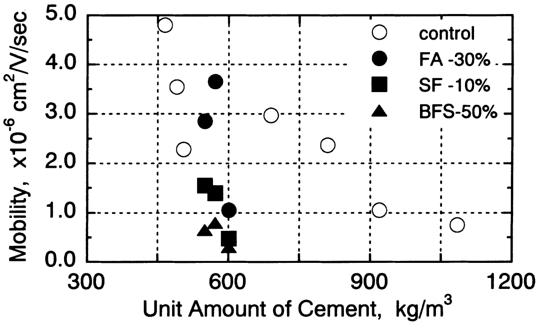

Fig. 7. Relation between amount of unit binder in hardened mortar and mobility of Cl^-.

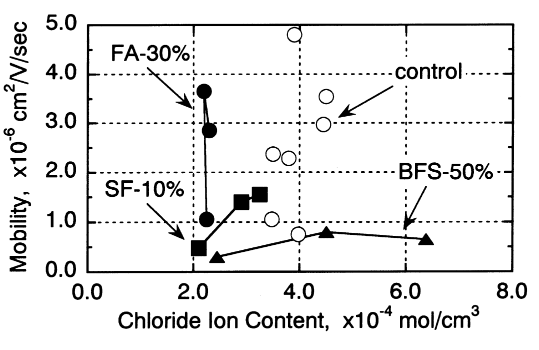

Fig. 8. Relations between Cl^- concentrations remaining in mortar of each mix proportion after charging and mobility of Cl^-.

6. Concluding remarks

This paper clarifies the effect of mineral admixtures in improving the properties of chloride ion migration. The major conclusions of this study are:

1. The mobility of Cl^- ion through mortars which contain silica fume or ground-granulated blast furnace slag is small for the same *W/B* and *S/C*.
2. Ground-granulated blast furnace slag controls the electro-chemical migration of Cl^- ion. However, Cl^- ion concentration in mortar is high after electric current was charged. Therefore, Cl^- ion may easily remain in mortar specimens.
3. Silica fume controls the electro-chemical migration of Cl^- ion. Furthermore, Cl^- ion concentration in mortar after charging is small compared to those without mineral admixtures. Therefore, Cl^- ion cannot easily remain in mortar specimens.
4. As for the fly ash, Cl^- ion concentration in mortar after charging is almost the same for silica fume. But, the effect which controls the electro-chemical migration of Cl^- ion is small.

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