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Communication

Relationship between the free and total chloride diffusivity in concrete

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Abstract

The relationship between the free and total chloride diffusivity in concrete is investigated using an electrochemical method established in our laboratory. The results show that the total chloride diffusivity is about 2.2–3.4 times the free one. It is assumed that the bound chloride content in concrete is about two times that of the free one.

Keywords: Chloride; Diffusion; Durability

1. Introduction

The chloride binding capacity of concrete may influence the durability of concrete in chloride containing environment [1–4]. It is known that the mineral admixtures, such as fly ash, slag, silica fume, etc., may increase the chloride binding capacity or decrease the chloride diffusivity in concrete. It is supposed that only the free chloride be capable of initiating the corrosion of reinforcement. The bound chloride should be harmless. This point of view is still controversial, not only on the definition of "free" and "bound," but also on the release of the bound chloride. In the present paper, the free chloride refers to the water-soluble chloride in concrete as usual, and the bound chloride means the total chloride minus the free one. The total chloride refers to the acid-soluble chloride in concrete.

It is recognized that the magnitude of chloride diffusivity in concrete not only can reflect the permeability of concrete, but also can be used to predict the service life of concrete as the model is based on the corrosion of steel bar [5]. So which one of the diffusivities mentioned above is to be used when evaluating the permeability and predicting the service life of concrete is very important. Different values may lead much different results. Nevertheless, it is being accepted that the free chloride diffusivity is the most important one. So major concerns should be how to determine the free chloride diffusivity in concrete and what is the relationship of the free and total chloride in concrete.

A method to determine the free and total chloride diffusivity in concrete has been established in our laboratory and the relationship between the free and total chloride diffusivity has been investigated in the present paper.

2. Experimental procedure

The free and total chloride in concrete are determined using an electrode couple of Ag/AgCl–SCE. Two calibrated curves are determined first. One is the electrode potential difference to chloride concentration in standard NaCl–$Ca(OH)_2$ solutions in which the $Ca(OH)_2$ is saturated. Another is the electrode potential difference to chloride concentration in standard NaCl–0.1 N HNO_3 solutions. The two plots are shown in Figs. 1 and 2. The accuracy using these two curves to determine the chloride concentration in the same type solutions is within 0.2%.

The free and total chloride profiles in concrete are determined as follows. After the concrete specimens ($100 \times 100 \times 300$ mm) are cured at 20 ± 2 °C (RH 90%) for 4 weeks, the top 20-mm was cut off and coated with wax, while leaving the newly cut surface uncoated, and then immersed in 3.5% NaCl solution. After 3 months of immersion, the specimen was drilled along the vertical direction from the uncoated surface using a driller with a powder collector. The collected powder was then placed in 50 ml of saturated $Ca(OH)_2$ or 0.1 N HNO_3 solution. The solution was stirred continually and kept for at least

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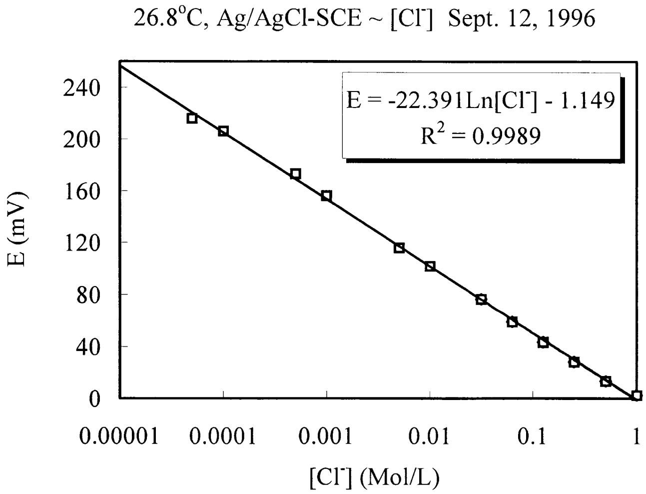

Fig. 1. The calibrated relationship between the potential difference of Ag/AgCl–SCE couple and the chloride concentration in NaCl–$Ca(OH)_2$ solutions.

48 h. The potential difference of the Ag/AgCl–SCE electrode couple was measured. The chloride concentration of the solution was calculated according to the calibrated equations and changed to that in concrete. The chloride concentration profile may be plotted after the variations of the chloride concentration with the concrete depths obtained. The free and total chloride diffusivities in concrete can be calculated using Fick's second law.

The concrete mixes are listed in Table 1.

Table 1
Concrete mix

Specimen	W/C	Portland cement (kg/m^3)	Fly ash (kg/m^3)	Slag (kg/m^3)	Sand (kg/m^3)	Coarse aggregate (kg/m^3)	Compressive strength at 28 days (MPa)
C1	0.40	486	–	–	588	1142	74.8
C2	0.45	454	–	–	588	1142	58.7
C3	0.50	427	–	–	588	1142	49.5
C4	0.55	402	–	–	588	1142	44.0
C5	0.60	380	–	–	588	1142	38.8
D1	0.40	413	73	–	588	1142	62.7
D2	0.50	363	64	–	588	1142	48.6
D3	0.60	323	57	–	588	1142	36.5
D4	0.40	364	122	–	588	1142	58.7
D5	0.50	320	107	–	588	1142	45.5
D6	0.60	285	95	–	588	1142	32.7
E1	0.40	340	–	146	588	1142	66.7
E2	0.50	299	–	128	588	1142	51.2
E3	0.60	266	–	114	588	1142	42.0
E4	0.40	243	–	243	588	1142	60.9
E5	0.50	214	–	214	588	1142	45.8
E6	0.60	190	–	190	588	1142	32.2

3. Results and discussion

The free and total chloride concentration profiles in some C series specimens are shown in Figs. 3 and 4. Typical chloride concentration profiles in fly ash and slag concrete are shown in Figs. 5 and 6, separately.

The relationship between the free and total chloride diffusivities in concrete is shown in Fig. 7. It is found that the total chloride diffusivity is times 2.2 to 3.4 to the free chloride diffusivity. The mathematical average is about 2.8. Considering the probability and error of measurements (see Fig. 8), it is assumed that the total chloride diffusivity is near 3.0 times the free chloride diffusivity. That is to say, the bound chloride content is about two times the free one. This rough relationship may be useful when predicting the

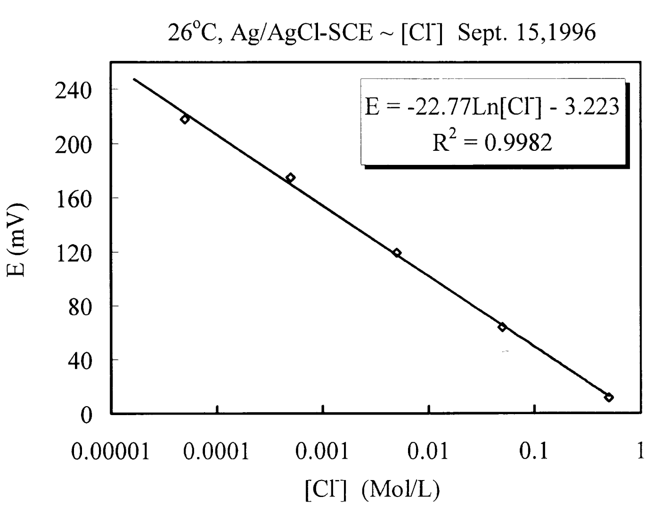

Fig. 2. The calibrated relationship between the potential difference of Ag/AgCl–SCE couple and the chloride concentration in NaCl–0.1 N HNO_3 solutions.

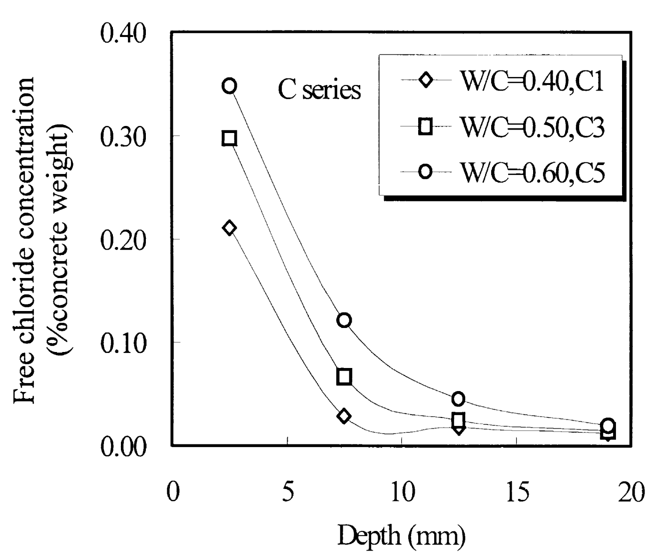

Fig. 3. Free chloride concentration profile in some C series specimens.

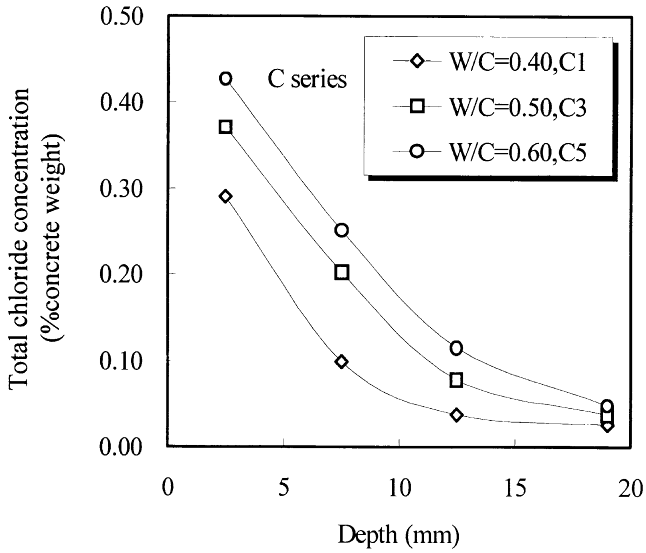

Fig. 4. Total chloride concentration profile in some C series specimens.

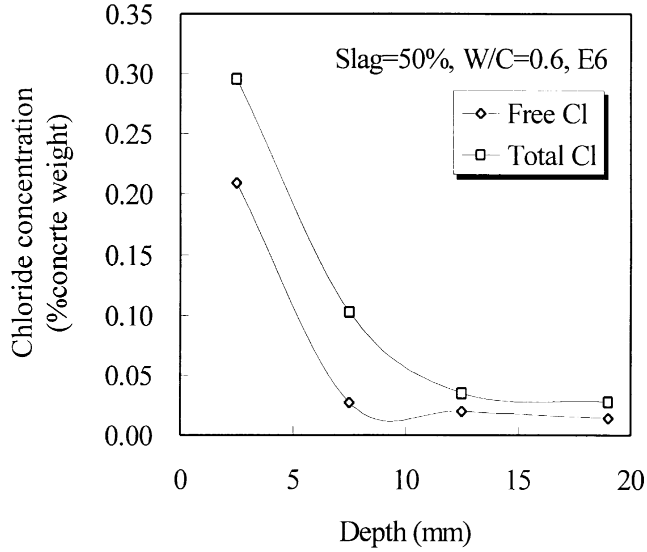

Fig. 6. Typical chloride concentration profile in slag concrete.

service life of concrete and comparing the permeability of concrete. It can be seen that, there may be three times difference produced when the total and free chloride diffusivities are used to predict the corrosion induction time of the same reinforcement. Now, it is being accepted that the free chloride diffusivity should be used when predicting the service life of concrete since the bound chloride is assumed harmless to the corrosion of rebar.

The mineral admixtures, like fly ash, ground blast furnace slag, and silica fume, cannot only decrease the permeability of concrete, but also decrease the free chloride and increase the bound chloride content in concrete. This effect is more obvious with the increase of the cement content and the water-to-binder ratio. The same result has been obtained in Ref. [2].

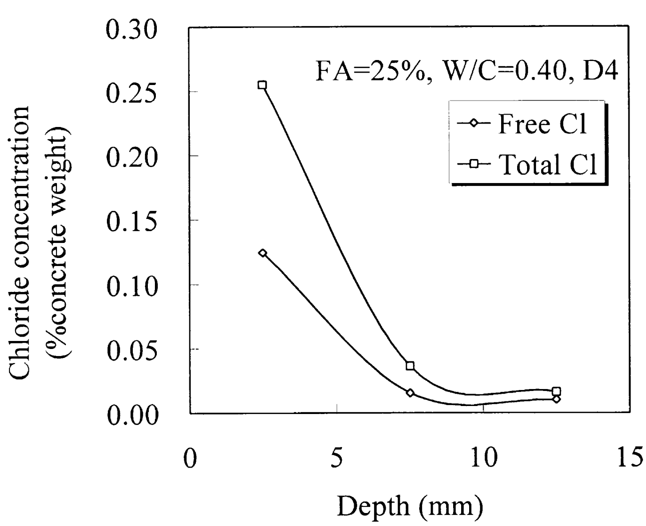

Fig. 5. Typical chloride concentration profile in fly ash concrete.

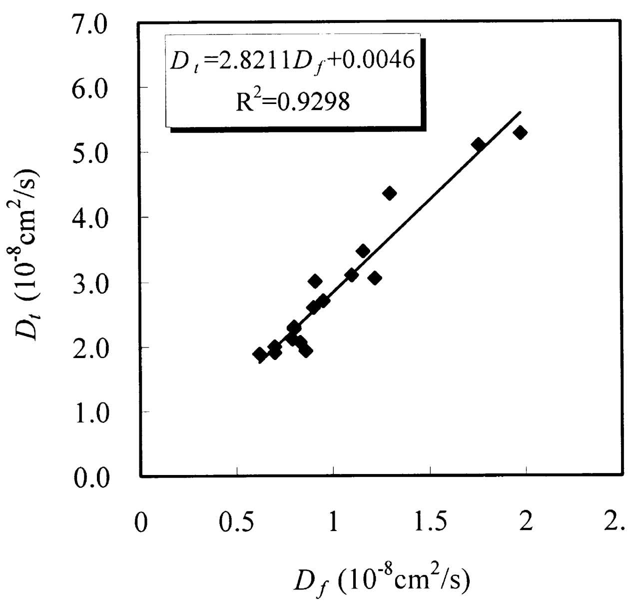

Fig. 7. The relationship between free and total chloride diffusivity in concrete.

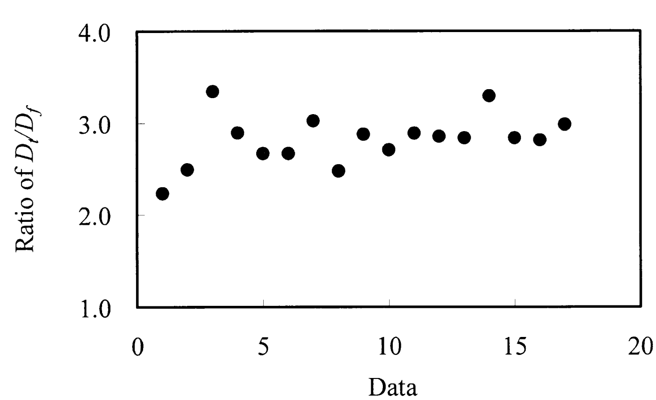

Fig. 8. Probability of ratio of D_t/D_F.

4. Conclusions

The total chloride diffusivity is about 2.2–3.4 times that of the free chloride in concrete. It is assumed that the bound chloride content in concrete is about two times that of the free one. This rough relationship may be useful when predicting the service life of concrete and comparing the permeability of concrete with different mineral admixtures when using the chloride diffusivity as permeability index.

Acknowledgments

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