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Communication

Determination of chloride diffusivity in concrete by AC impedance spectroscopy

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Abstract

A new method of determination of the diffusion coefficient D of chloride in concrete has been proposed. It has been shown that the AC impedance technique is a powerful tool for the determination. For most simple electrochemical reactions, a Nyquist plot of AC impedance spectra are of the Randles type, which is characterized by a straight line of slope 1 in the low-frequency region. Impedance of diffusion known as Warburg impedance Z_W can be obtained from the intersection of the straight line on the real axis. From the coefficient of Warburg impedance Z_W, the diffusion coefficient can be calculated. For determination of the chloride diffusion coefficient, a special ideal nonpolarizable electrochemical reaction was chosen. The results are in good agreement with those reported in the literature. The advantage of the new method lies in its simplicity and reproducibility. Due to changes in microstructure, it was found that the diffusion coefficient of chloride in concrete changes with time in the hydration process.

Keywords: Cement paste; Chloride; Diffusion

Chloride diffusivity and permeability of concrete are of great importance for the durability of concrete. They are mostly measured by direct electrical methods [1–5]. The AC impedance method is a powerful tool used in studying stationary as well as transient processes in a system. For electrochemical systems, the kinetics and mechanisms of reactions can be elucidated. Dynamics of mass transfer under a concentration gradient, known as diffusion, can also be studied. Concrete specimens, immersed in chloride solution of a certain concentration for a sufficient period of time to guarantee that all the pores in the microstructure are filled with the solution and capillary paths are established for diffusion, can be considered to be an electrochemical system that can be studied by the AC impedance method.

1. Theoretical background

The AC impedance technique has long been used in the study of electrochemical reactions. For a general electrochemical reaction of $O + \mathrm{ne} \leftrightarrow R$ by measuring the frequency response of the impedance Z, much information about the reaction mechanism and mass transfer can be obtained. Experimental data are often plotted in a complex plane known as a Nyquist plot. Typical Nyquist plots are of the Randles type as shown in Fig. 1. Their analytical expressions are shown in Eqs. (1), (2), and (3):

$$Z = R_s + \frac{Z_F}{1 + i\omega Z_F C_d} \tag{1}$$

$$Z_F = R_{ct} + Z_W \tag{2}$$

$$Z_W = \sigma\omega^{-1/2}(1 - i) \tag{3}$$

in which ω is the angular frequency, $\omega = 2\pi f$, R_s is the resistance of electrolytic solution, and C_d is the capacitance of the electrode/electrolyte interface. The reaction kinetics and diffusion are characterized by Faradaic impedance Z_F, which is composed of the resistance of charge transfer R_{ct} in series with the so-called Warburg impedance Z_W describing the diffusion behavior. They can be represented by the equivalent circuit as shown in Fig. 2.

In Fig. 2 it can be seen that for the Randles case, in the high-frequency region the experimental curve is a semicircle and in the low-frequency region it is a straight line of slope 1. Correspondingly, at the high-frequency limit, Warburg impedance Z_W becomes unimportant, and Eq. (1) will be reduced to Eq. (4):

$$Z = R_s + \frac{R_{ct}}{1 + i\omega R_{ct} C_d} \tag{4}$$

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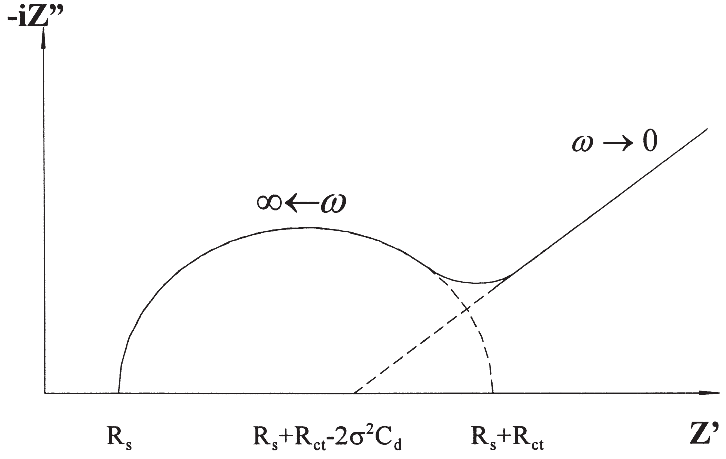

Fig. 1. Nyquist plot of an electrochemical reaction of Randles type.

at the low frequency limit it will approach the limiting form shown in Eq. (5) and Eq. (6):

$$Z' = R_s + R_{ct} + \sigma\omega^{-1/2} \quad (5)$$

$$Z'' = \sigma\omega^{-1/2} + 2\sigma^2 C_d \quad (6)$$

Elimination of ω leads to Eq. (7):

$$Z'' = Z' - R_s - R_{ct} + 2\sigma^2 C_d \quad (7)$$

where σ is the coefficient of Warburg impedance, which can be obtained from the intersection of the straight line on the real axis. Another way to measure σ is based on the so-called Randles plot, a plot of the real part and the imaginary part of Z_F against $\omega^{-1/2}$ (see Fig. 3). σ can be obtained from the slope of two parallel lines. Z_F can be extracted from Z by subtraction from the equivalent circuit [6].

For a reversible reaction, $R_{ct} \to 0$ and the two parallel lines become one and intersect the origin (Fig. 4). This can be viewed as the criterion of the reversibility of the reaction in Eq. (6). σ in Eqs. (5) and (6) is the coefficient of Warburg impedance and is related to diffusion coefficients D_O and D_R as shown in Eq. (8):

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{D_O^{1/2}C_O} + \frac{1}{D_R^{1/2}C_R}\right) \quad (8)$$

where R is the gas constant, T is the absolute temperature, F is Faraday’s constant, A is the area of electrode surface, D_O and D_R are diffusion coefficients of oxidized state O and reduced state R respectively, and C_O and C_R are concentrations of O and R [6].

Eq. (8) can be deduced by solving the partial differential equation of Fick’s second law under certain initial and boundary conditions. As there are two different diffusion coefficients D_O and D_R involved in Eq. (8), for our purpose of determination of chloride diffusion alone we must choose a suitable reaction, as in Eq. (9):

$$\mathrm{Ag} = \mathrm{Cl}^- \Leftrightarrow \mathrm{AgCl} + e \quad (9)$$

This is a typical reversible reaction, which is controlled by diffusion of chloride ion alone. In this reaction silver and silver chloride are in the solid phase; chloride ions alone in a certain spatial distribution of concentration remain in the solution and diffuse under a concentration gradient. By similar deduction, we have Eq. (10):

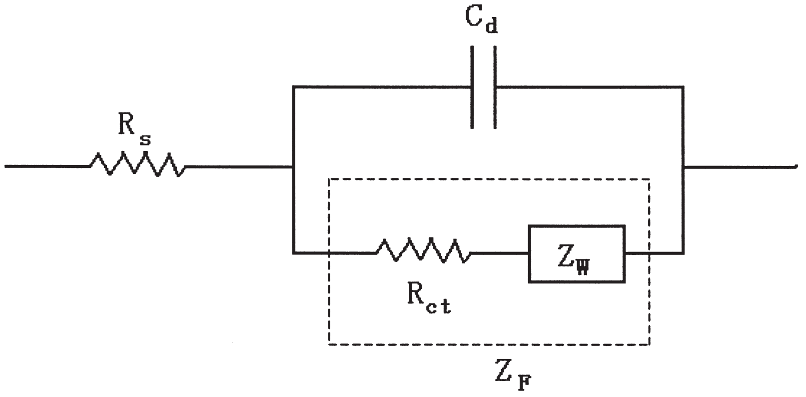

Fig. 2. Equivalent circuit of Fig. 1.

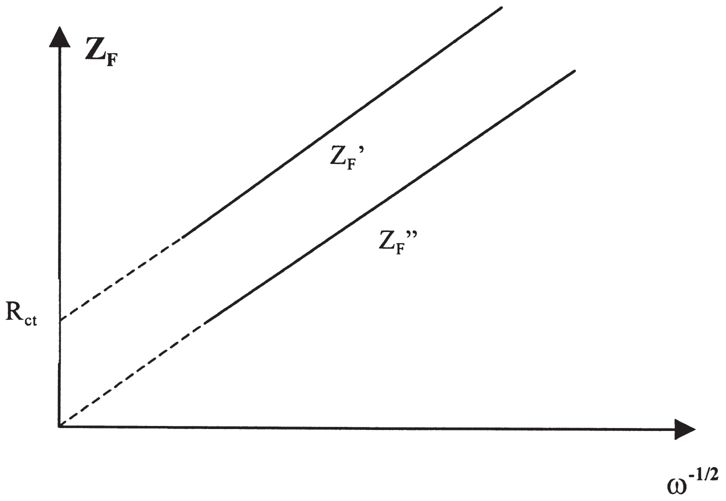

Fig. 3. Randles plot of Z_F' and Z_F''.

$$\sigma = \frac{RT}{F^2 A\sqrt{2}D^{1/2}C} \tag{10}$$

hence, EQ. (11):

$$D = \left(\frac{RT}{\sqrt{2}F^2\sigma C}\right)^2 \tag{11}$$

For $t = 25°\text{C}$, we have Eq. (12):

$$D = 3.54 \times 10^{-14}(A\sigma C)^{-2} \tag{12}$$

If we put a concrete specimen fully immersed in chloride solution between two silver electrodes, by the same procedure, σ and hence the diffusion coefficient of chloride ion in concrete can be determined with great accuracy.

2. Methods

2.1. Specimens

Cements pastes with water/cement ratios of 0.5 and 0.25, respectively, were cast in molds of 20 × 20 × 20 mm and cured for 24 h at a relative humidity >95%. Afterward the specimens were immersed in NaCl solution of different concentrations for more than 2 days. Cubic specimens of concrete, 100 mm on each side, were also prepared. The mix proportions of the concrete are summarized in Table 1.

2.2. Electrodes

Two porous silver electrodes were prepared by electroplating silver in $KAg(CN)_2$ solution on silver plate of 20 × 20 mm.

2.3. Technique and equipment

The two porous silver electrodes were put opposite each other in close contact with the specimen. Impedance measurement were performed by a Potentiostat/Galvanostat M273A connected with Lock-in Amplifier M5210 manufactured by EG&G PARC (Princeton Applied Research Co., USA). Measurement and data processing were supported by software M398 afforded by the same manufacturer. Amplitude of the sinusoidal voltage was chosen to be 10 mV. The technique of Fast Fourier Transform (FFT) was applied at low-frequency range from 0.1 to 11.31 Hz.

3. Results and discussion

Specimens of 20 × 20 × 20 mm mortar with water/cement ratio of 0.5 were immersed in chloride solution of different concentrations. Randles plot of the specimens is shown in Fig. 5. From Fig. 5 it can be seen that there are straight lines of different slopes for all four cases. The coefficient of diffusion impedance *s* can be obtained from the slopes of these lines. To check the validity of Eq. (12), the plot of σ vs. 1/C is shown in Fig. 6.

Impedance spectra of specimens with water/cement ratio of 0.25 and 0.5 immersed in 0.5 M NaCl solution were mea-

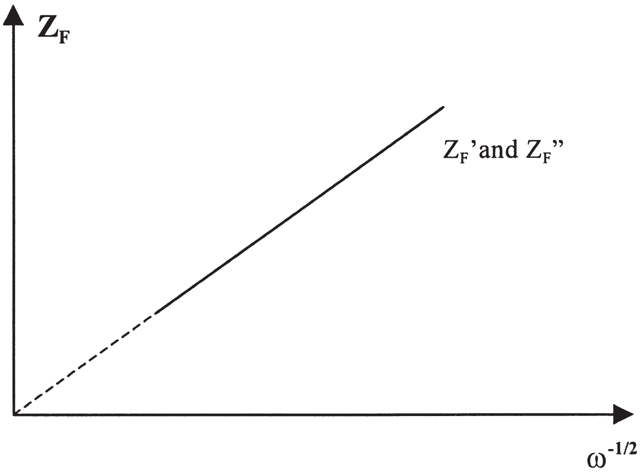

Fig. 4. Randles plot of a reversible reaction.

Table 1
Concrete mixtures

Concrete[a]	Specimen no.	Mix proportions kg/m^3 OPC	PFA	SF	Water	Aggregates 0–5 mm	6–15 mm	w/c + f	Compressive strength MPa (design)
OPC	C30	375	–	–	180	645	1200	0.48	30
	C40	460	–	–	180	615	1145	0.39	40
	C60	583	–	–	175	673	1010	0.30	60
OPC/PFA	CF7	470	164	–	186	669	962	0.29	70
OPC/SF	CS7	478	–	72	165	692	1036	0.30	70

[a] OPC = ordinary Portland cement; PFA = pulverized fuel ashes; SF = silica fume.

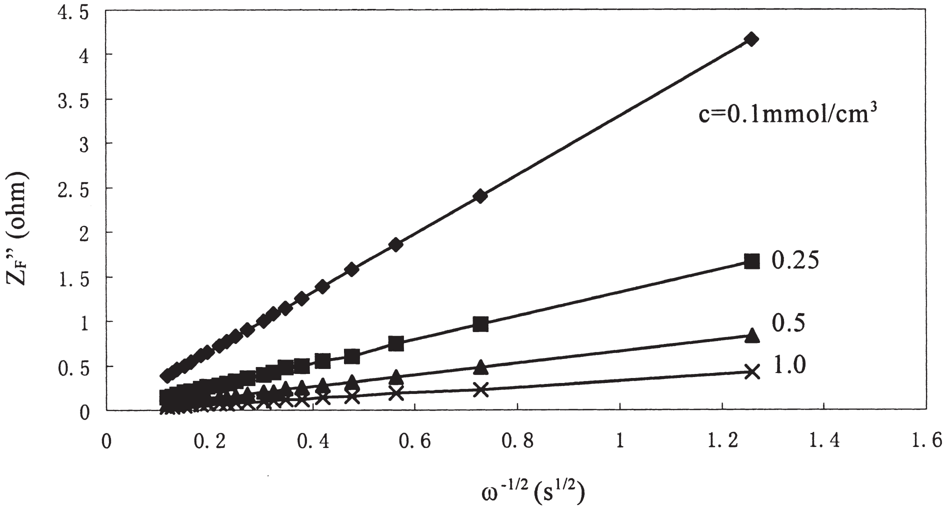

Fig. 5. Randles plot of mortar with water/cement ratio of 0.5 in NaCl solution of different concentration.

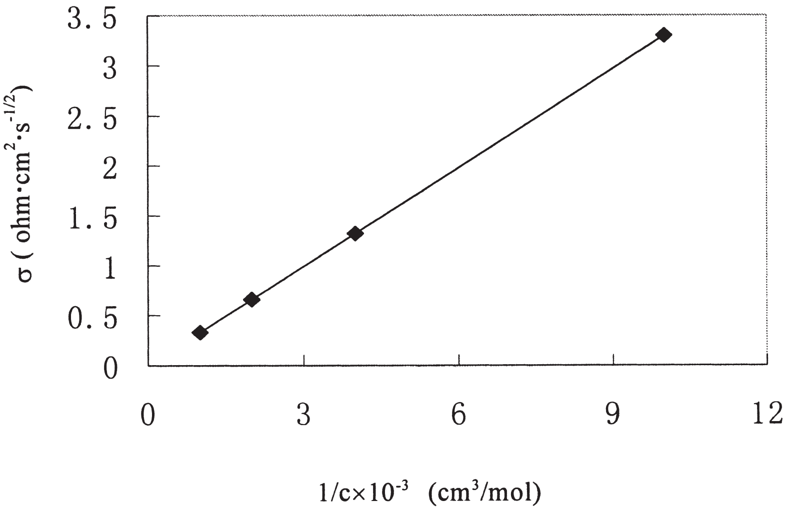

Fig. 6. Plot of σ vs. 1/*C* for mortars with water/cement ratio of 0.5.

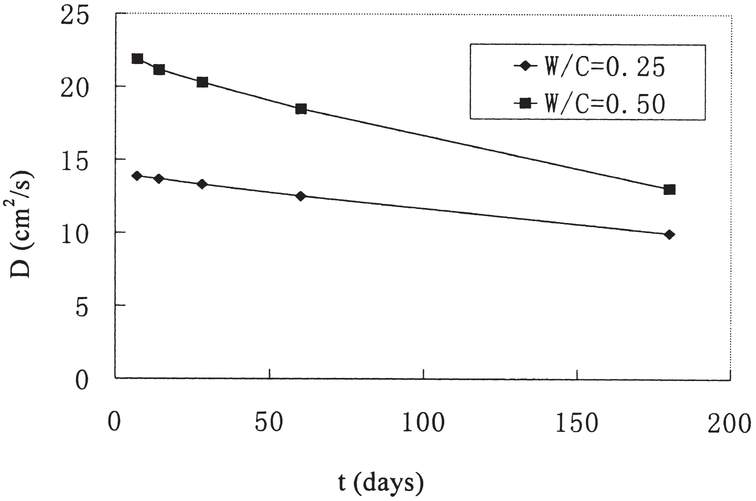

Fig. 7. Change of chloride diffusion coefficients with time.

sured at different times of hydration. The results are shown in Fig. 7. From Fig. 7 it can be seen that diffusion coefficient of chloride in mortars with water/cement ratio of 0.5 is greater than that of 0.25. With the increase of hydration time, chloride diffusion coefficient becomes smaller. An empirical relation may be established as seen in Eq. (13):
In the above-mentioned cases, for mortars with water/cement ratio of 0.25, $D_0 = 14.1 \times 10-9$ cm^2/s, $\tau = 528.9$ days, and for mortars with water/cement ratio of 0.5, $D_0 = 22 \times 10 \times 9$ cm^2/s, $\tau = 345$ days.

The results of measurement on concrete are summarized in Table 2.

$$D = D_0 e^{-t/(\tau)} \tag{13}$$

Table 2
Coefficient of chloride diffusion after 28 days curing

	Specimen				
Specimen no.	C30	C40	C60	CF70	CS70
σ ($\Omega \cdot$ cm$^2 \cdot$ s$^{-1/2}$)	0.593	0.695	0.918	1.718	1.962
D $\times$ 10^9 (cm^2/s)	25.2	18.3	10.5	3.0	2.3

4. Conclusion

Different from DC methods for the measurement of chloride diffusivity, which are based on ion migration under electrical field, the AC impedance technique is proposed to measure the diffusion of chloride ions in a quasi-static state. As diffusion itself, rather than other quantities, are measured, the results should be more reliable.

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