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APPLICATION OF THE NERNST-EINSTEIN EQUATION TO CONCRETE

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ABSTRACT

Theoretical application of the Nernst-Einstein equation to the determination of diffusivities of aggressive ions in concrete, establishment of rapid tests for the permeability of concrete, monitoring the corrosion of reinforcement, and predicting the service life of reinforced concrete structures are mainly discussed. It is shown that (1)When the transference number of an ion is known or designated to be approximately 1.0, the diffusivity of this ion in concrete can be easily obtained from the Nernst-Einstein equation by measuring the partial conductivity of this ion or the total conductivity of the concrete; (2)The permeability of concrete can be evaluated by the conductivity of concrete when saturated with concentrated salt and the Nernst-Einstein equation is employed. (3)Corrosion of reinforcement can be easily monitored or predicted by measuring the concrete conductivity change, when the Nernst-Einstein equation is combined with the corrosion mechanisms. (4)If the reinforced concrete structure is to be designed durable for more than 100 years, the diffusion coefficients of chloride and oxygen should be no larger than the magnitude of $10^{-9}cm^2/s$, and the thickness of the concrete cover and the diameter of reinforcement should be no less than 25mm and 10mm, respectively. © *1997 Elsevier Science Ltd*

Introduction

Transportation of aggressive ions in concrete has a great influence on the durability of concrete (1). For example, the ingress of chloride and sulfate ions may cause the corrosion of reinforcement and the deterioration of concrete. Therefore, the diffusion coefficient or diffusivity of aggressive ions may be one of the most important parameters for evaluating the durability or predicting the service life of a concrete structure (2).

Several methods have been put forward to determine the diffusivity of chloride (3~15). Some are based on Fick's law and use a 'diffusion cell' (3~8), and others on the Nernst-Plank equation and use a 'migration cell' (9~15). Theoretical fundamentals associated with these methods have been discussed elsewhere in detail (16~19).

Although many people have become interested in the migration test, very few workers have recognized the importance of the relationship between the diffusion and electromigration of ions in the same electrolyte. Therefore, a not new but quite simple approach to determine the diffusivity of aggressive ions in concrete, particularly for chloride ions, which is based on the Nernst-Einstein equation, has been put forward (2). This approach has also been employed to evaluate the permeability of concrete, monitor the corrosion of reinforcement, and predict the service life of the reinforced concrete structure. The theoretical aspects and applications of this approach are discussed in the present work.

Relationship Between Diffusivity of Aggressive Ions and Conductivity of Concrete

Diffusion of aggressive ions has an important influence on the durability of concrete and the corrosion of reinforcement. After concrete hardened, the diffusion of aggressive ions is predominantly controlled by the composition and the microstructure of the concrete. Of course, same as any other physicochemical process, it is also influenced by temperature, pressure, ion type, and other factors. As the composition and microstructure of concrete may change with time owing to interaction with the environment, the diffusion of ions is a time-dependent process. It is difficult to predict the diffusion coefficient of ions in a long period, but rapid tests may be established to determine the diffusivity at any time, and this is what the present work concerns.

Diffusion is usually described phenomenologically by Fick's law (20). In spite of weather the process is in steady state or not, it can be formulated as,

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial^2 x} \tag{1}$$

which is called the Fick's second law; where, C_i is the concentration of species i at distance x at time t, D_i is the diffusion coefficient of i. The solution to equation [1] is,

$$C_i(x,t) = C_{i0}\left(1 - erf\frac{x}{2\sqrt{D_i t}}\right) \tag{2}$$

where, $C_i(x,t)$ is the concentration of species i at distance x and time t, C_{i0} is the concentration of species i at $x = 0$. It should be known that, when Fick's law is used to describe the diffusion process, it is with the following assumptions: (1)The fluxing species must not react with the matrix, (2)The matrix is homogenous in structure and composition. From equation [2], it can be seen that if the concentration of ions in the environment and the diffusivity of the concrete are known, the penetrating profile at any time can be computed. Otherwise, if the concentration profile is known, the diffusivity of ions can be calculated from equation [2], assuming a value for C_{i0}; this method is commonly used but can be time-consuming.

If concrete is considered to be a solid electrolyte, the diffusivity of charged species i in concrete is related to its partial conductivity σ_i, and this relation is called the Nernst-Einstein equation (21),

$$D_i = \frac{RT\sigma_i}{Z_i^2 F^2 C_i} \tag{3}$$

where, D_i is the diffusivity of species i (cm^2/s); R is the gas constant (8.314J/mol · K); T is absolute temperature (K); σ_i is partial conductivity of species i (S/cm); Z_i is the charge of species i; F is Faraday's constant (96500 Coul/mol); C_i is the concentration of species i (mol/cm^3).

If the partial conductivity σ_i and the concentration C_i have been determined, the diffusivity of species i, D_i, can be calculated from equation [3]. The partial conductivity σ_i is,

$$\sigma_i = t_i \sigma \tag{4}$$

where, σ is the conductivity of concrete; t_i is the transference number of species i, which is defined as,

$$t_i = \frac{Q_i}{Q} = \frac{I_i}{I} \tag{5}$$

where, Q_i, I_i are the electric quantity and current contribution of species i to the total electric quantity Q and current I, respectively.

If the diffusivity of an ion is to be determined by the Nernst-Einstein equation, the transference number of this ion should be known. A simple and proper approach is to make the transference number equal or approximate to 1.0, though it is not exactly right. For example, if the chloride diffusivity is to be determined, the concrete can be filled with a concentrated salt solution. At this condition, the transference number of chloride may be assumed as 1.0, and C_i may be considered equal to the chloride concentration in the pore solution, or the solution used to fill the concrete. When T = 298K, C_{Cl} = 0.005mol/cm^3, for example, the relationship calculated for chloride diffusivity and concrete conductivity is shown in Fig. 1. When concrete conductivity is varying from 0.1 to 4.0 × 10^{-3}s/cm, the calculated diffusivity of chloride is changing from 5.32 × 10^{-9} to 2.13 × 10^{-7}cm^2/s. This is consistent with the pub-

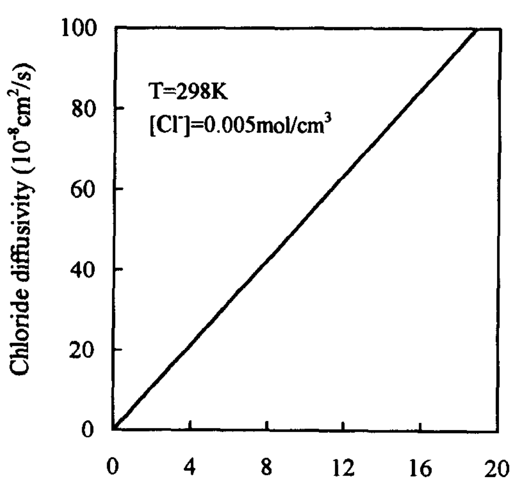

FIG.1
Calculated relationship between chloride diffusivity and concrete conductivity.

TABLE 1

Concrete conductivity from Ref. (25) and chloride diffusivity calculated from Eqt. [3]

Water/Cement ratio	0.3	0.4	0.5	0.6	0.7	0.8
σ_{OPC}(ms/cm)	-	1.5	2.0	2.5	3.0-3.5	3.5-4.0
$\sigma_{OPC\text{-}30\%PFA}$(ms/cm)	0.5	0.5-1.0	1.0-1.5	1.5-2.0	2.0-2.5	2.5-3.0
$D_{Cl\text{-}OPC}$(10^{-8}cm^2/s)	-	7.98	10.6	13.3	16.0-18.6	18.6-21.3
$D_{Cl\text{-}OPC\text{-}30\%PFA}$($10^{-8}$cm^2/s)	2.66	2.66-5.32	5.32-7.98	7.98-10.6	10.6-13.3	13.3-16.0

lished results obtained from laboratory and field data for ordinary concrete, Portland cement paste and mortar (3~15, 22~24).

The conductivities in Table 1 are from reference (25) for concrete which was cured for 28 days and saturated with 5M NaCl solutions. The chloride diffusivity in Table 1 is calculated from equation [3], presuming C_{Cl} = 0.005mol/cm^3 and T = 298K. The calculated data is in reasonable agreement with the results of Page and coworkers (3, 10). This may lead to the conclusion that the diffusion coefficients of aggressive ions in concrete can be assumed by the conductivity of the concrete which is saturated with a suitable salt containing such ions.

Rapid Test for Permeability of Concrete to Aggressive Ions

Permeability of concrete is considered to be the essential index for evaluation of the durability of concrete (26). Several rapid tests for permeability of concrete have been established, but no test can be applicable to all types of penetrating media. Therefore, it is difficult to compare the data obtained from the different tests for different media.

Permeability of concrete, considered by the author, is one of the intrinsic properties of concrete; it is only associated with the structural and chemical properties of the concrete, not the media studied. Thus the data obtained from any rapid test may demonstrate the same property of the concrete, even though they might be in different units. As the penetrating of an aggressive medium without pressure is a diffusion process, and the permeability of concrete is usually consistent with the diffusivity of the medium investigated, the diffusion coefficient of this medium is considered to be an exact reflection of the permeability of concrete.

Chloride is a well-known aggressive substance in concrete, and some rapid tests for its permeability have been established (11, 12, 22, 25, 27), while others are still in development (2, 25). Most of the methods put forward have one or more shortcomings. For example, in the AASHTO T277 test (27), a high voltage (60V) is employed, and the heat produced during the test may have a bad influence on the microstructure of the concrete and the results obtained. The index provided by AASHTO T277 is the electric quantity passed though the concrete during 6 hours; it doesn't easily remind people of the intrinsic property of the permeability of concrete.

As some people have also recognized the diffusivity of chloride is a good reflection of the permeability of concrete, they developed some rapid tests, which might be called 'accelerated diffusion' or 'migration' tests, to calculate the chloride diffusivity in concrete (11, 12, 22). However, these tests are essentially based on the idea that an electric field can accelerate the migration of chloride through concrete, the relationship between the diffusion and electromigration having been ignored. Fortunately, a new rapid test has been formulated by Streicher and Alexander according to the Nernst relation (25), and a similar test has been put forward by the present author based on the Nernst-Einstein equation(2), i.e., the relationship between diffusion and electromigration.

The big differences of our rapid test from the others are: (1)It converts the chloride permeability determination to the conductivity measurement of the concrete which is saturated with a highly concentrated salt (NaCl, usually). It is based on the idea that the permeability of concrete could be evaluated by the diffusivity of chloride, and the determination of chloride diffusivity could be transferred to the concrete conductivity measurement when the Nernst-Einstein equation is employed. (2)The voltage applied is low enough to eliminate the bad effects caused by a high voltage after concrete is filled with salt. (3)The influence of the reaction of chloride with hydration products can be neglected when concrete is saturated with salt. The information obtained only reflects the behavior of the free chloride ions. (4)The influence of absorption process occurring during the other tests can be erased. (5)Very short time is used, even for high strength concrete. (6)Since diffusivity is not dependent on the concentration, highly concentrated solutions can be used during the test to increase the accuracy of measurements and calculations.

The empirical relationship between the chloride diffusivity and conductivity and permeability of concrete, which was established based on the published and calculated data (1~15, 22~25), is given in Table 2. It can be seen that, when the concrete strength is high enough, and water/cement ratio is low, the chloride diffusivity changes from about 5×10^{-10} to $5 \times 10^{-9} cm^2/s$, and the concrete has a low permeability to chloride. That is to say, high performance concrete should have a conductivity in the range of 0.01~0.1ms/cm or even smaller, i.e., the resistivity is 1000~100Ωm or even larger, when it is saturated with salt. Similarly, ordinary concrete may have a conductivity in the range of 0.5~2.5ms/cm, i.e., the resistivity is 20~4Ωm. The poor concrete might have a conductivity in the range of 3~4ms/cm, i.e., the resistivity is 2.5~3.3Ωcm. Therefore, it sounds like the permeability of concrete might be quickly evaluated by the conductivity of concrete when the Nernst-Einstein equation is employed to calculate the diffusivity of chloride in concrete.

Estimation and Monitoring the Corrosion of Reinforcement

Corrosion of reinforcement is usually caused by the carbonation of concrete and accumulation of chloride at the concrete/reinforcement interface. The transportation of aggressive media is usually the controlling step for the corrosion of reinforcement. Therefore, the diffusion coefficients of aggressive media, such as carbon dioxide, chloride and oxygen, are most important to estimate the corrosion of reinforcement and the service life of a concrete structure. After the diffusivities of the corrosive media are determined, the corrosion rate of reinforcement and its service life may be estimated from corrosion models (2, 28).

It has been known that the diffusivity of corrosive medium can be conveniently determined by measuring the conductivity of concrete when proper experiments are designed. For example, if the corrosion of reinforcement is induced by chloride, the chloride diffusivity may be determined by measuring the conductivity of the concrete which is saturated with NaCl. The induction time, i.e., the period needed to reach the chloride threshold, can be estimated from equation [2]. If the threshold of chloride is defined as $[Cl^-] / [OH^-] = 0.6$ at the surface of steel (29, 30), though it is questionable (31, 32), $[Cl^-]_0 = 3.5$wt% NaCl≈0.62mol/l (sea water), pH = 13 at the surface of the reinforcement, the thickness of concrete cover is varied as 25, 50, or 100 mm, and the chloride diffusivity is varied as listed in Table 2, and provided it is determined by the concrete conductivity measurement, then the

TABLE 2

Conductivity and Permeability of Concrete and Diffusivity of Chloride

f_c(MPa)	W/C	σ(ms/cm)	D_{Cl}(10^{-8}cm^2/s)	Permeability
>60	<0.3	0.01	0.0532	Excellent
		0.05	0.266	
		0.10	0.532	
30~60	0.3~0.6	0.50	2.66	Good
		1.0	5.32	
		1.5	7.98	
		2.0	10.6	
		2.5	13.3	
<30	>0.6	3.0	16.0	Poor
		3.5	18.6	
		4.0	21.3	

calculated induction times are shown in Fig. 2. It can be seen that, if the concrete is designed to be durable for several decades, the chloride diffusivity can be no larger than the magnitude of 10^{-9}cm^2/s, i.e., the conductivity of concrete when saturated with concentrated salt must be smaller than 0.1ms/cm. Considering the results published, the strength of concrete must be higher than 60MPa and W/C < 0.3.

According to the corrosion models established (2), when corrosion of reinforcement is controlled by the diffusion of oxygen, the corrosion current of reinforcement can be estimated by the following equation,

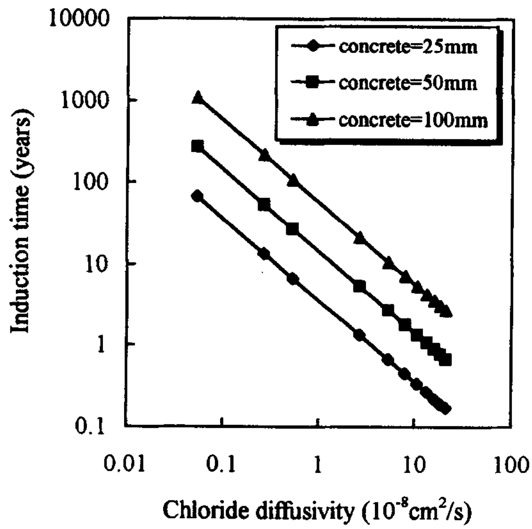

FIG. 2.
Relationship between calculated induction time and chloride diffusivity.

TABLE 3

Diffusion Coefficients of Chloride and Oxygen in Concrete from Ref. (10)

W/C	D_{Cl} (10^{-8}cm^2/s)		D_o (10^{-8}cm^2/s)	
	OPC	OPC+30%PFA	OPC	OPC+30%PFA
0.4	3.95	0.39	9.33	5.79
0.5	7.80	0.43	10.40	6.67
0.6	12.60	0.90	13.64	7.51
0.7	21.46	1.03	21.75	8.88

$$i_{corro} = i_{diff} = nF\ D_o \frac{[O_2]}{\delta} \tag{6}$$

where, i_{corro} is the corrosion current of reinforcement; i_{diff} is the critical diffusion current of oxygen; n is the electrons lost of oxygen during the cathodic reaction; D_o is the diffusion coefficient of oxygen in the diffusion layer; $[O_2]$ is the soluble oxygen concentration at the outside surface of the diffusion layer; δ is the effective thickness of the diffusion layer on the reinforcement surface. If the corrosion reached steady state, D_o and $[O_2]$ in equation [6] may be considered equal to that of in the pore solution. As $[O_2]$ and δ might be considered as constants, the corrosion rate of the reinforcement is directly related to the diffusivity of oxygen. When the corrosion rate of reinforcement and index for concrete failure are known, the propagation time, i.e., the period from corrosion beginning to concrete failure, can be estimated from the corrosion model.

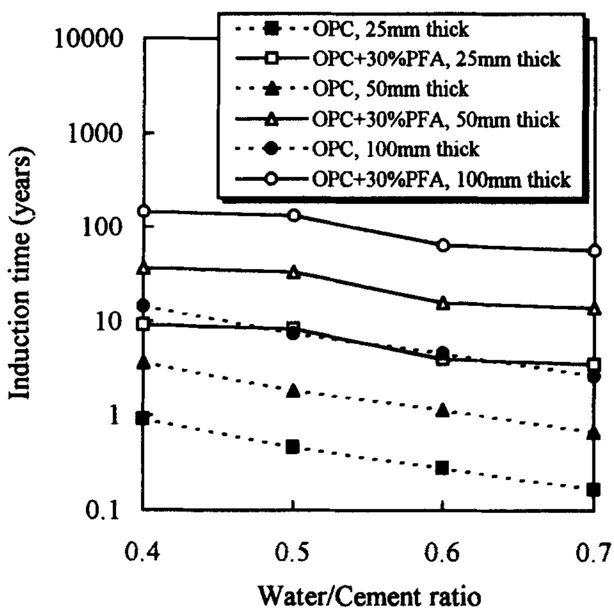

FIG. 3.
Relationship between estimated induction time and W/C ratio.

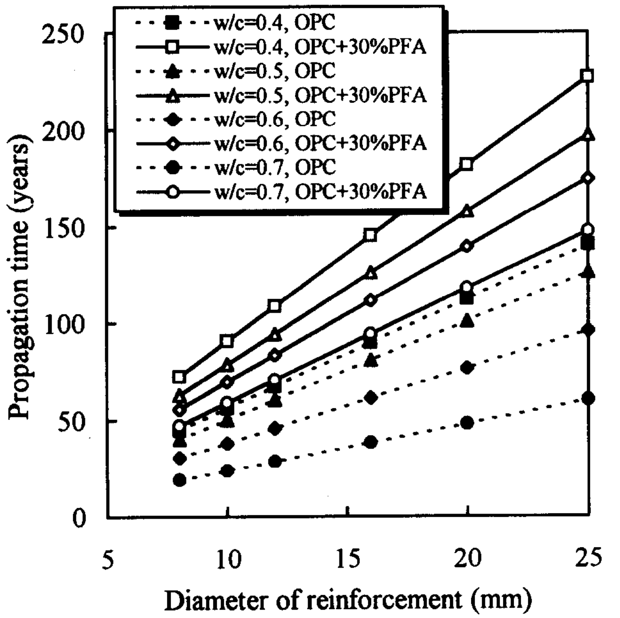

FIG. 4.
Relationship between estimated propagation time and diameter of reinforcement.

Table 3 shows the diffusion coefficients of chloride and oxygen in concrete obtained by Page and coworkers (10). Fig. 3 and Fig. 4 are the estimated induction and propagation times corresponding to the data in Table 3, when the failure of structure is indexed by 5% loss of the cross section of the reinforcement, $[O_2] = 10^{-7}$mol/cm^3, $\delta = 10^{-3}$cm (33), and the diameter of the reinforcement is varied from 8 to 25mm. It can be seen that, if the concrete is to be designed durable for more than 100 years, the diffusion coefficients of chloride and oxygen should be no larger than the magnitude of 10^{-9}cm^2/s, the thickness of concrete cover and the diameter of reinforcement ought to be large enough, no less than 25mm and 10mm respectively, and also that proper addition of mineral admixtures, such as fly ash, is greatly beneficial to the durability.

From the Nernst-Einstein equation, it is known that the more conductive concrete is, the more rapid transportation of aggressive ions, then the faster the corrosion of steel. Therefore, through the examination of the concrete conductivity change, the corrosion of reinforcement may be easily predicted. The Linear Polarization method is one of the rapid tests for corrosion, which is based on the Stern-Geary equation (34), i.e.,

$$i_{corro} = \frac{b_a b_c}{2.303(b_a + b_c)} \cdot \frac{1}{R_p} = \frac{B}{R_p} \tag{7}$$

where, b_a and b_c are Tafel constants for anodic and cathodic reaction, respectively; B is usually in the range of 6.5~52mV for corrosion of metals in liquid solutions, for steel in concrete, B is usually amounted 26mV for active, and 52mV for passive; R_p is called linear polarization resistance. According to the simplified equivalent circuit for a corroding reinforced concrete system (35, 36), when R_p consists of the concrete and the interfacial resistance, then equation [7] is changed to,

$$i_{corro} = \frac{B}{R_{concr} + R_{inter}} \tag{8}$$

Since concrete resistance (R_{concr}) is dependent on the electrolyte and water in concrete and interfacial resistance (R_{inter}) is dependent on the surface state of reinforcement, the corrosion current may be varied with the penetration of aggressive ions, and the progressing corrosion. Therefore, through monitoring the resistance change, the diffusion of ions and corrosion of reinforcement and the damage of concrete may be predicted. According to equation [8], it can also be known that, if the concrete resistance is large enough, for example, when the concrete has a high density, low permeability, little salt content and free water, i.e., a small water/cement ratio, and a high strength, the corrosion current of the reinforcement may be neglected. This may be one of the reasons why a high performance concrete should be developed.

If the Nernst-Einstein equation is combined with the Stern-Geary equation, a simple in-situ monitoring technique might be easily developed to predict the beginning of the corrosion of reinforcement and the damage of the concrete structure by measuring the conductivity change of concrete.

Summary

According to the calculations and discussions above, it can be known that (1)When the transference number of an ion is known or designated to be approximately 1.0, the diffusivity of this ion in concrete can be easily obtained from the Nernst-Einstein equation by measuring the partial conductivity of this ion or the total conductivity of the concrete; (2)The permeability of concrete can be evaluated by the conductivity of concrete when saturated with concentrated salt and the Nernst-Einstein equation is employed. (3)Corrosion of reinforcement can be easily monitored or predicted by measuring the concrete conductivity change, when the Nernst-Einstein equation is employed and combined with the corrosion mechanisms. (4)If the reinforced concrete structure is to be designed durable for more than 100 years, the diffusion coefficients of chloride and oxygen should be no larger than the magnitude of $10^{-9}cm^2/s$, and the thickness of the concrete cover and the diameter of reinforcement should be no less than 25mm and 10mm, respectively.

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