Pergamon

Cement and Concrete Research, Vol. 25, No. 7, pp. 1535-1542, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00147-6

EFFECT OF IONIC INTERACTION IN MIGRATION TESTING OF CHLORIDE DIFFUSIVITY IN CONCRETE

Tiewei Zhang and Odd E. Gjørv

Division of Building Materials
The Norwegian Institute of Technology - NTH
N-7034 Trondheim - NTH, Norway

(Refereed)
(Received February 1; in final form May 4, 1995)

ABSTRACT

The actual drift velocity of chloride ions in concrete measured by migration testing in concentrated NaCl solutions not only depends on the applied electric field but also on the ionic interaction. A net velocity V_d is calculated considering the relaxation and electrophoretic effects of the ionic cloud around an ion described by the Debye-Hückel theory. V_d is dependent on ionic concentration, ionic mobility, applied electric field, and other parameters. A correction factor, β^0, which is the ratio of the ideal to the actual drift velocity of ions, is calculated for NaCl solutions up to 0.5 M. Higher salt concentrations do not permit correction since the Debye-Hückel theory is invalid when the thickness of ionic cloud is comparable to the average hydrated ionic radius. The correction factor permits calculation of the actual chloride diffusion coefficient during testing by introducing a concentration related retardation in ion migration velocity of up to 41% for a 0.5 M NaCl solution at 20°C.

INTRODUCTION

According to the ionic cloud or Debye-Hückel theory (1-3), a certain interaction between ions in ionic aqueous solutions always exists due to the properties and structural characteristics of the electrolyte molecules. The stronger the ionic concentration, the stronger is the ionic interaction. Above a certain concentration, the interaction may become so strong that both the chemical potential and the transport behavior of the ions are significantly affected. Thus, for increasing concentration of chloride ions in a salt solution to which concrete is exposed, the effect of ionic interaction may significantly retard the rate of chloride diffusion. Hence, a concentration dependent diffusion coefficient is observed. Also, for the same chloride concentration, a change in other types of ions in the external salt solution may introduce other types of ionic interaction. Thus, by changing the type of cation from sodium to calcium, a significantly increased rate of chloride diffusion into concrete is observed (4).

Over recent years, various methods for accelerated testing of chloride diffusivity in concrete have been introduced. By use of strong chloride solutions, however, calculation of diffusivity based on conventional diffusion theory may no longer be applicable without any correction or modification. Also in migration testing, the ionic clouds surrounding the chloride ions will produce dragging forces in such a way that the rate of chloride movement towards the electrode is retarded.

In a previous paper, a correction for ionic interaction in migration testing of chloride diffusivity from NaCl solutions of various concentrations was introduced (5). In the present paper, the background for introducing such a concentration dependent correction is presented.

General

The ionic interaction is partly due to the interaction between the individual ions and partly due to the interaction between the ions and the solvent molecules. According to the Debye-Hückel theory, the ion-ion interaction can be described as a formation of an oppositely charged ionic atmosphere (ionic cloud) surrounding the central ions of interest. This ionic cloud lowers the electric potential of the ions and thus retards the drift velocity. Under the action of an external electric field, the ionic interaction will result in two different effects:

(1) The electrophoretic effect, which is the resulting action of the external field on the ionic clouds oppositely charged compared to the central ions, and the action between these ionic clouds.

(2) The relaxation effect, which is the distortion of the ionic clouds when the central ions move towards the electrode.

Therefore, in addition to the dominant electric driving force there also are some other forces acting on the moving ions. Both the resultant operating force and the individual components may be illustrated as shown in Fig. 1. Here, F^0 is the electric driving force, and V^0 is the drift velocity of the ions in an ideal dilute solution, while the subscripts E and R represent the components of the electrophoretic and the relaxation effect, respectively. F_d and V_d are the resultant driving force and drift velocity, respectively. Both the electrophoretic and the relaxation forces are always in the opposite direction to that of the electric driving force. Hence, the motion of the ions towards the electrode is retarded.

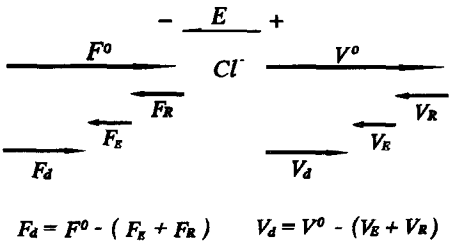

Fig. 1. Components of driving force and drift velocity of a migrating ion.

The electrophoretic effect

As long as the ions are not infinitely apart, the central ions will experience a viscous drag as they move through the solution. The ions with their charged clouds will also carry along their clusters of solvent molecules rubbing past each other, thus enhancing the viscous drag and lowering the drift velocity.

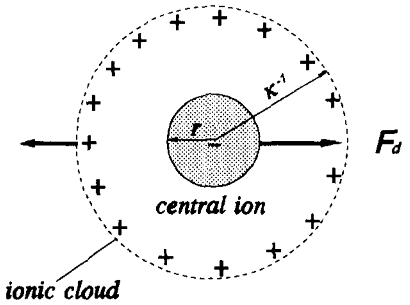

Fig. 2. The electrophoretic drag force caused by an ionic cloud.

The oppositely charged ionic atmosphere is accelerated by the external electric force which is of same magnitude as that on the central ion, but retarded by the Stokes viscous force of the solution (Fig. 2).

When a steady-state velocity V_E is obtained, the viscous force is exactly equal and opposite to the electric driving force:

$$ze_0\frac{E}{300} = 6\pi\kappa^{-1}\eta V_E \qquad (1)$$

where e_0= charge of proton
z = ionic valence
E = external electric field
κ^{-1}= radius of the ionic cloud (the radius of the diffusing particle r, is replaced by κ^{-1} because the ionic cloud is taken into consideration)
η = viscosity.

From Eq. (1), the electrophoretic drag on the drift velocity of the ion can be expressed as:

$$V_E = \frac{ze_0}{6\pi\kappa^{-1}\eta}\cdot\frac{E}{300} \qquad (\mathrm{cm.s^{-1}}) \qquad (2)$$

The relaxation effect

When the central ion moves, the ionic atmosphere around it lags behind and is distorted. This distortion produces an extra field (the relaxation field), which produces a relaxation force acting on the central ions. The following expression for the relaxation force F_R and the relaxation velocity V_R have been developed (2):

$$F_R = \frac{ze_0^3\kappa\omega}{6\varepsilon kT}\cdot\frac{E}{300} \qquad (\text{dyne.ion}^{-1}) \qquad (3)$$

and

$$V_R = \frac{u^0 e_0^2\kappa\omega}{6\varepsilon kT}\cdot E \qquad (\text{cm.s}^{-1}) \qquad (4)$$

where u^0= conventional ionic mobility in infinite dilute solution
ε = dielectric constant (permittivity)
k = Boltzmann constant
ω = Onsager correction factor (for 1:1 electrolyte, T=25°C, ω=0.5859)
κ^{-1}= Debye-Hückel reciprocal length (the radius of ionic atmosphere). For 1:1 electrolyte, κ can be calculated from the following equation:

$$\kappa = \left(\frac{8\pi z^2 e_0^2 c}{\varepsilon kT}\right)^{1/2}.\left(\frac{N_A}{1000}\right)^{1/2} \qquad (\text{cm}^{-1}) \qquad (5)$$

where c is the molar concentration of the electrolyte and N_A is Avogadro constant.

From the above equation it can be seen that the ionic interaction depends on several parameters. The two dragging forces V_E and V_R are both related to the type of electrolyte and to the concentration of the electrolyte through the radius of the ionic cloud κ^{-1}. The dielectric constant ε also depends on the ion concentration. Further, all parameters are temperature dependent.

Net velocity of ionic migration

The above outline of transport mechanisms provides a basis for an analysis of both the conductivity of an electrolytic solution and the effect of ionic interaction on the migration velocity of the ionic species. In the following, however, only the effect of ionic interaction on the migration velocity is considered.

From Fig. 1 the resultant force F_d acting on the ions and the net velocity V_d can be expressed as follows:

$$F_d = F^0 - (F_E + F_R) \qquad (6)$$

and

$$V_d = V^0 - (V_E + V_R) \qquad (7)$$

where F^0 is the driving force from the applied electric field, and V^0 is the drift velocity of the ions in an infinite dilute solution without any ionic interaction.

By introducing Eq.(2) and Eq.(4) into Eq.(7), the following expression can be obtained:

$$V_d = V^0 - \left(\frac{ze_0}{6\pi\eta} + \frac{300u^0 e_0^2\omega}{6\varepsilon kT}\right).\kappa.\frac{E}{300} \qquad (\text{cm.s}^{-1}) \qquad (8)$$

where V^0 and u^0 represent the values of drift velocity and "conventional mobility" of the ions in an infinite dilution under the action of an electric field, respectively. The conventional mobility is determined as:

$$u = \frac{V}{E} \tag{9}$$

where V is the drift velocity of the ions and E is the applied electric field. If u^0(ionic mobility in infinite dilute solution) is known, V^0 can be calculated from Eq. (9). u^0 can either be obtained from Stock's equation (2-3) or from the following relationship:

$$\lambda^0 = z.u^0.F \tag{10}$$

where λ^0 is the conductivity of an individual ionic species at infinite dilution, which can be obtained from relevant text books, and F is the Faraday constant. Since for NaCl z=1, V^0 for Cl^- can be obtained as follows:

$$V^0 = u^0 E = \frac{\lambda^0}{F} \cdot E \tag{11}$$

By introducing Eq.(11) into Eq.(8), the effect on ionic interaction can be obtained in the form of net velocity. Eq.(8) demonstrates that for a certain type of electrolyte, the ion concentration plays an important role since both the dielectric constant ε and the radius of the ionic atmosphere κ^{-1} are concentration dependent. Again, the temperature plays an important role.

CORRECTION FOR IONIC INTERACTION

According to the above analysis, the actual drift velocity of an ionic species under the action of an applied electric field is smaller than it should be due to the effect of ionic interaction. Therefore, a correction factor β^0 can be introduced, which is the ratio of the ideal to the actual drift velocity of the ions:

$$\beta^0 = \frac{V^0}{V_{act}} \tag{12}$$

where V_{act} is the actual net-drift velocity of the ions. In the previous paper (5), the measured "equivalent" drift velocity V_{eq} of the chloride ions in the migration system corresponds to V_{act}.

It should be noted that the Debye-Hückel theory is generally considered to be valid only when the effective thickness of the ionic cloud κ^{-1} is far larger than the average hydrated ionic radius $\boldsymbol{a}$, i.e. $\kappa^{-1} >> \boldsymbol{a}$ (6). Since the value of $\boldsymbol{a}$ for chloride ions in NaCl solutions is about 4 Å, the corresponding maximum concentration at which the ionic cloud is compacted to the same size is about 0.58 M. Therefore, corrections were only made for concentrations of up to 0.5 M.

Since from Eq. (9), $V^0 = u^0.E$, Eq. (8) can be expressed in the following form:

$$V = AE - BE \tag{13}$$

where

$$A=u^0 \tag{14}$$

and

$$B = \left(\frac{ze_0}{6\pi\eta}+\frac{50u^0e_0^2\omega}{\varepsilon kT}\right)\frac{\kappa}{300} \tag{15}$$

Then, the ratio V^0/V is:

$$\frac{V^0}{V} = \frac{AE}{AE-BE} = \frac{A}{A-B} \tag{16}$$

which shows that the correction factor β^0 is independent of the applied electric field E.

The theoretical relationship between the chloride diffusion coefficient D and the migration velocity of chloride ions has previously been obtained by applying the Einstein equation (5):

$$D = 300\frac{kT}{ze_0E}\,V_d \qquad (\mathrm{cm^2.s^{-1}}) \tag{17}$$

Since this equation is based on the assumption of an infinite dilute solution where $V_d=V_{eq}=V^0$, while the practical testing is carried out on concentrated solutions where $V_{eq}=V_{act}<V^0$, a correction for ionic interaction is necessary. Such a correction can be made by introducing the correction factor β^0 (Eq. 12) into Eq. (17):

$$D = \beta^0{\cdot}300\frac{kT}{ze_0E}\,V_{act} \tag{18}$$

When the test parameters are introduced (5), Eq.(18) becomes:

$$D = \beta^0\frac{300kT}{ze_0\Delta\psi}\cdot\frac{LV}{c_0A_0}\cdot\frac{dc}{dt} \tag{19}$$

This equation can further be re-written as

$$D = \beta.\alpha.\frac{dc}{dt} \tag{20}$$

where the factors β and α include all the universal constants and the necessary test parameters, respectively:

$$\beta = \beta^0\frac{300k}{ze_0} \tag{21}$$

$$\alpha = \frac{T}{\Delta\psi}\cdot\frac{LV}{c_0A_0} \tag{22}$$

The improved calculation of diffusivity based on steady-state migration testing can either be based on Eq. (18) or on Eq. (19). In Table 1, the correction factors β^0 and β have been calculated for some NaCl solutions with chloride ion concentrations of up to 0.5 M, while the relevant constants and test variables used in the calculation are shown in Table 2.

From Table 1 it can bee seen that when the concentration of the chloride source solution is increased from 0.1 to 0.5 M at 20°C, the effect of ionic interaction will retard the migration velocity of the chloride ions by approximately 18 and 41%, respectively. At 25°C, the retardation will be by up to 45%. For higher chloride concentrations, a correction for ionic interaction cannot be made since the ionic cloud or the Debye-Hückel theory is no longer valid.

Table 1. Correction factors for ionic interaction of chloride ions from NaCl solutions of different concentrations and temperatures.

c_0 (NaCl) mol/l	$\beta^0=V^0/V$					
	20°C	21°C	22°C	23°C	24°C	25°C
0.1	1.22	1.23	1.23	1.24	1.24	1.25
0.2	1.35	2.36	1.37	1.37	1.38	1.39
0.3	1.47	1.48	1.49	1.50	1.51	1.53
0.4	1.58	1.59	1.61	1.63	1.64	1.66
0.5	1.70	1.71	1.74	1.76	1.78	1.80
c_0 (NaCl) mol/l	$\beta=\beta^0.300k/ze_0$ ($\times10^{-4}$)					
	20°C	21°C	22°C	23°C	24°C	25°C
0.1	1.06	1.06	1.06	1.07	1.07	1.08
0.2	1.16	1.17	1.18	1.19	1.19	1.20
0.3	1.26	1.27	1.29	1.29	1.30	1.32
0.4	1.36	1.37	1.39	1.40	1.42	1.43
0.5	1.46	1.48	1.50	1.52	1.53	1.55

CONCLUSIONS

In the present paper, it is shown that ionic interaction represents an important effect which has to be taken into account for calculation of chloride diffusivity based on migration testing. A correction factor is introduced, which permits calculation of the actual chloride diffusion coefficient during testing. This correction factor introduces a concentration related retardation of the ion migration velocity by up to 41% for a 0.5 M NaCl solution at 20°C. By taking this effect into account, a more basic approach to the use of diffusivity as a general quality parameter for evaluation of concrete durability is obtained.

Table 2. Universal constants and test parameters.

Symbol	Physical meaning	Values for calculation
e_0	Charge of proton	4.8×10^{-10} esu.
z	Ionic valence	For Cl^-: z=1
k	Boltzmann constant	1.38×10^{-16} ergs.K^{-1}.ion^{-1}
R	Gas constant	8.31 J.K^{-1}.mol^{-1}
F	Faraday constant	96480 C.mol^{-1}
ε	Dielectric constant	For NaCl: $\varepsilon \approx 80 - 10.c$ (c: mol/l)
η	Viscosity of H_2O (20°C-25°C)	$\lg(\eta_{25}/\eta)=\{1.37[t-20]+8.36.10^{-4}[t-20]\}/(109+t)$ (g.cm.s^{-1})
λ^0	Standard ionic conductivity	For Cl^- : $\lambda^0=76.34$ Ω^{-1}.cm^2.mol^{-1}
u^0	Standard ionic mobility	For Cl^- : $u^0=\lambda^0/F=7.912\times10^{-4}$ sec^{-1}.V^{-1}
ω	Onsager correction constant	0.59 (For 1:1 electrolyte, 25°C)
c_0	Source Cl^- concentration	mmol.cm^{-3} (mol.l^{-1})
c	Cl^- concentration in collecting cell	mmol.cm^{-3} (mol.l^{-1})
$\Delta\psi$	Applied electric potential	Volt
L	Distance between electrodes	cm
E	Electric field ($E=\Delta\psi/L$)	volt.cm^{-1}
dc/dt	Rate of Cl^- concentration increase in collecting cell	mmol.cm^{-3}.sec^{-1}
V	Volume of collecting cell	cm^3
A_0	Cross section area	cm^2
T	Absolute temperature	T=273+t(°C) K
t	Time	sec.

REFERENCES

(1) Debye, D. and Hückel, E., Zeitschrift für Physik, Vol. 24, 1921.

(2) Bockris, J.O.M. and Reddy, A.K.N.," Modern Electrochemistry", 3rd Edition, Plenum Press, New York, 1977.

(3) Atkins, P.W., "Physical Chemistry", 5th Edition, Oxford University Press, Oxford, 1994.

(4) Gjørv, O.E. and Vennesland, Ø., "Evaluation and Control of Steel Corrosion in Offshore Concrete Structures", Katharine and Bryant Mather International Conference on Concrete Durability, Proceedings, J.M. Scanlon (Ed.), ACI SP-100, Vol. 2, 1987, pp. 1575-1602.

(5) Zhang, T. and Gjørv, O.E.,"An Electrochemical Method for Accelerated Testing of Chloride Diffusivity in Concrete", Cement and Concrete Research, Vol. 24, 1994, pp. 1534-1548.

(6) Newman, J.S.,"Electrochemical Systems", Prentice Hall, Englewood Cliffs, New Jersey, 1991.

(7) Sørensen, H. and Fredriksen, J.M., "Testing and Modelling of Chloride Penetration into Concrete", Nordic Concrete Research, Research Projects 1990, Oslo, 1990, pp. 354-356.

(8) Gjørv, O.E., "Important Test Methods for Durability of Reinforced Concrete", M. Malhotra Symposium on Concrete Technology - Past, Present and Future, Proceedings, P.K. Mehta (Ed.), ACI SP-144, 1994, pp. 545-574.