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DIFFUSION BEHAVIOR OF CHLORIDE IONS IN CONCRETE

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ABSTRACT

In the present paper, an analysis of the diffusion behavior of chloride ions in concrete is presented. In concentrated electrolytic aqueous solutions such as seawater or that typically used in laboratory experiments, the effect of ionic interaction may significantly reduce the chemical potential and thus the driving force of the diffusing species. Because of different drift velocities of the cations and chloride ions in the solution, the lagging motion of the cations will also retard the drift velocity of the chlorides. In addition, both the electrical double layer forming on the solid surface and the chemical binding may significantly interfere with the transport of the chloride ions. As a result, the diffusion behavior of the chloride ions in concrete is a more complex and complicated transport process than what can be described by Fick's law of diffusion.

Introduction

Transport of chloride ions inside a moist concrete is commonly assumed to be governed by a diffusion process which obeys Fick's law of diffusion. During testing of chloride diffusivity, however, a diffusion behavior is often observed which cannot be explained by Fick's law. Long-term testing shows that the apparent diffusivity is not constant(1-2). Also, a change in type of external salt solution, even though the chloride ion concentration is kept the same, may significantly affect the rate of chloride ingress into the concrete(3-6).

The diffusion behavior of chloride ions in concrete is affected by a number of factors which are partly related to the characteristics of the concrete and partly to the composition of the external salt solution. Very often, all these effects are ignored. In chloride salt solutions such as that typically used in laboratory experiments, the effect of ionic interaction may lower the chemical potential and thus the diffusing driving force of the chloride ions. In addition, other effects in the diffusion system such as the lower drift velocity of cations relative to anions, the electrical double layer forming on the pore walls as well as the pore volume and pore sizes of the material may also affect the diffusion behavior to a great extent.

In two previous papers, the effect of ionic interaction was discussed and taken into account in migration testing of chloride diffusivity in concrete(7-8). In the present paper, a more complete analysis of the diffusion behavior of chloride ions in concrete, is presented.

Reduction in Chemical Potential

The chemical potential of a species i is given by(9-11):

$$\mu_i = \mu_i^0 + RT\ln a_i \tag{1}$$

where
μ_i^0 = chemical potential of the solute i in the standard state (J/mol)
a_i = activity of species i (molar concentration identical, i.e. $c_0 = 1$ molar)
R = gas constant (8.314 J/mol.K)
T = absolute temperature (K)

For a hypothetical system of ideal (non-interacting) particles, the activity of a species can be considered to be equal to its concentration, and hence, its chemical potential can be expressed as(9-10):

$$\mu_i(\text{ideal}) = \mu_i^0(c) + RT\ln c_i \tag{2}$$

where c_i is the molar concentration of the species i.

The diffusing driving force of species i in a unit volume for a one-dimensional diffusion comes from the gradient of its chemical potential(10):

$$F_d = -c_i\frac{d\mu_i}{dx} = -RT\frac{dc_i}{dx} \tag{3}$$

and the steady-state diffusing flux J (mass/unit area) is:

$$J \propto F_d = -BRT\frac{dc_i}{dx} \tag{4}$$

where B is the proportionality. Thus, the *diffusion coefficient* D can be expressed as:

$$D = BRT \tag{5}$$

For a given temperature, the diffusion coefficient D is a constant, and Eq. (4) becomes Fick's first law (12-13).

However, for an electrolytic solution or a *real solution*, $a_i \neq c_i$. By introducing a correction factor $\gamma_i = a_i/c_i$, called *activity coefficient*, where γ_i is the molar activity coefficient, Eq. (1) becomes(9-10):

$$\mu_i(\text{real}) = \mu_i^0(c) + RT\ln c_i + RT\ln \gamma_i \tag{6}$$

Then, the driving force becomes:

$$F_d = -RT\frac{dc_i}{dx}\left(1 + \frac{d\ln\gamma_i}{d\ln c_i}\right) \tag{7}$$

and the flux is:

$$J = -BRT \frac{dc_i}{dx}\left(1 + \frac{d\ln\gamma_i}{d\ln c_i}\right) \tag{8}$$

Thus, the diffusion coefficient D can be expressed as:

$$D = -BRT \frac{dc_i}{dx}\left(1 + \frac{d\ln\gamma_i}{d\ln c_i}\right) \tag{9}$$

The diffusion coefficient is then dependent upon the *activity coefficient* of the diffusing species.

The *Debye-Hückel theory*(9-11) or the "ionic-cloud theory" ascribes the change in chemical potential to the ion-ion interaction in the solution. In this theory, an arbitrarily selected ion is considered as a *reference ion* or *central ion*, while the remaining ions in the solution are considered as the *ionic atmosphere* or *ionic cloud* surrounding the central ion. The solvent molecules provide a dielectric medium, while the surrounding ions give rise to an excessive or net charge density. Thus, the total charge in the atmosphere must be of opposite sign and exactly equal to that of the central ion. A positively charged ion has a negatively charged ionic cloud and vice versa. By using this model, a quantitative evaluation of the ionic interaction in an electrolytic solution becomes possible. The effective *thickness of the ionic cloud*, or the *Debye length* κ^{-1} is then given as:

$$\kappa = \left(\frac{N_A e_0^2}{500\,\varepsilon\,\varepsilon_0 kT}\right)^{1/2} \cdot I^{1/2} = B \cdot I^{1/2} \tag{10a}$$

where

$$B = \left(\frac{N_A e_0^2}{500\,\varepsilon\,\varepsilon_0 kT}\right)^{1/2} \tag{10b}$$

where

κ = reciprocal of Debye length (m^{-1})
N_A = Avogadro constant (6.022×10^{23}/mol)
k = Boltzmann constant ($k = R/N_A = 1.38 \times 10^{-23}$ J/K)
e_0 = charge of proton (1.602×10^{-19} C = 4.8×10^{-10} esu)
ε = dielectric constant of the solution
ε_0 = permittivity of the medium in vacuum (8.854210×10^{-14} F/cm)
I = ionic strength

From Eqs. (2) and (6), the potential change for a real solution $\Delta\mu_{i\text{-}I}$ is:

$$\Delta\mu_{i\text{-}I} = \mu_i(\text{real}) - \mu_i(\text{ideal}) = RT\ln\gamma_i \tag{11}$$

where $\ln\gamma_i$ is also given by the Debye-Hückel theory as follows(9-11):

$$\ln \gamma_i = -\frac{N_A (z_i e_0)^2}{8\pi \varepsilon \varepsilon_0 RT}\left(\frac{\kappa}{1 + a\kappa}\right) = -A\frac{1}{\varepsilon} \cdot \frac{\kappa}{1 + a\kappa} \tag{12a}$$

where
R = gas constant (8.314J/mol.K)
z_i = ionic valence
κ^{-1} = Debye length (m)
a = ion size parameter

and

$$A = N_A (z_i e_0)^2 / 8\pi \varepsilon_0 RT \tag{12b}$$

As can be seen from Eq. (10), the Debye length is controlled by several characteristics of the solution such as type of electrolyte, concentration of solution and ionic valence. Fig.1 shows the plot of the relationship between the Debye length and the concentration of the electrolyte, from which it can be seen that Debye length for a 1:1 type of electrolyte is always larger than that of a 1:2 type of electrolyte.

In addition, the dielectric constant e is also a function of the solution concentration. For some electrolytic aqueous solutions such as that of NaCl, an approximately linear relationship exists for low concentrations:

$$\varepsilon = \varepsilon_0 - \beta c \tag{13}$$

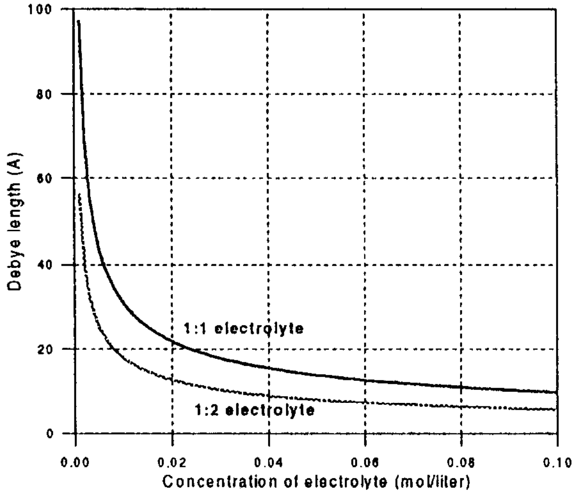

FIG. 1.
Relationship between Debye length and concentration of electrolyte.

From the above, it can be seen that the activity coefficient of a species depends on both κ and ε, which reflect the effect of ionic interaction in the system. When $|d\ln\gamma_i/d\ln c_i \ll 1$ for a given solution, the diffusing driving force is a mono-function of the concentration gradient, and the diffusion coefficient D can be considered to be a constant. Hence, Fick's law becomes a good approximation.

By considering chloride ions being the diffusing species and differentiating Eq. (12) with respect to its concentration c_i combined with Eqs. (11) through (13), a change in the chemical potential of the chloride ions can be calculated for solutions of binary salts such as NaCl and $CaCl_2$. Fig. 2 shows the plots of some calculated results.

From Fig. 2 it can be seen that in chloride solutions, the chemical driving force of chloride ions decreases rapidly for increasing concentration of the electrolyte, indicating that even at very low concentrations the effect of ionic interaction is strong enough to significantly reduce the chemical driving force of the ionic species. Therefore, for most chloride concentrations practically used for testing of chloride diffusivity in concrete, even at an early stage of the diffusion process when the chloride concentration inside the concrete is very low, the diffusion behavior of the chlorides may deviate from Fick's law, and hence, the apparent diffusion coefficient will not be a constant.

Although the Debye-Hückel theory is valid only for very diluted solutions, this theory appears to provide a valuable basis for a qualitative analysis.

Retardation of Drift Velocity

The response of an ion to a driving force is identified by its *mobility*, where the "*absolute mobility*", u_{abs}, is defined as (10):

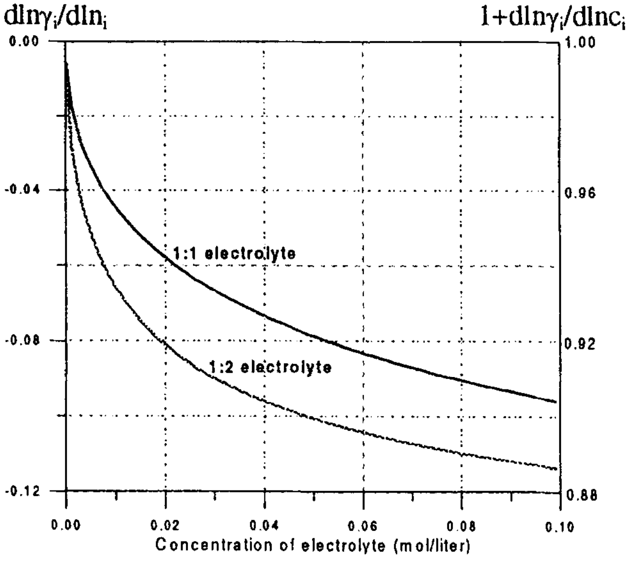

FIG. 2.

Change in chemical potential of chloride with increase of concentration of electrolyte.

$$u_{abs} = \frac{v_d}{F_d} \quad (14)$$

where, v_d is the drift velocity and F_d is the driving force (i.e. chemical or electrical). In the study of conductance of ions, a more convenient parameter, *conventional mobility*, is used, which is defined as the drift velocity v_d under a unit electrical field E (10-11):

$$u = \frac{v_d}{E} \quad (15)$$

It should be noted that the *mobility* of ions is a transport parameter in the same way as the diffusion coefficient. The relationship between these two parameters is given by the Einstein equation (10):

$$D = u_{abs}\,kT \quad (16)$$

In a diffusion or a migration process, the cations and anions usually move at different velocities in the electrolytic solutions due to their different mobility. Therefore, an electrostatic action between the cations and anions will occur. As a result, the observed diffusion coefficient of a single ion represents the resultant diffusion of both cations and anions (11).

Since a diffusion of the chloride ions also must be accompanied by a diffusion of the cations from the same salt, and the cations usually move at a slower rate than the anions, a lagging motion of the cations will act as a dragging force on the diffusing chloride ions. Hence, a retarded diffusion rate of the chlorides will be observed. This is the reason why the observed diffusivity of a salt D from a binary electrolyte is a function of the diffusion coefficients for both the cations and the anions:

$$D = f(D_+, D_-) \quad (17)$$

For conventional testing of chloride diffusivity in concrete, it is generally observed that the diffusion coefficient for chlorides is affected by both type of salt and type of cations(3-6). For example, if the cation in the external salt solution is changed from sodium to calcium while the chloride ion concentration is kept the same, an increased chloride diffusivity by a factor of up to 2 to 3 may be observed. Such a phenomena can partly be explained by a higher dragging force created by the sodium ions compared to that of the calcium ions.

Effect of Electrical Double Layer

In solid-electrolytic solution systems, the formation of an electrical double layer on the solid surface is also an important phenomenon, a model of which is shown in Fig. 3. The surface potential y_0 is determined by the rigidly adsorbed ions or the *potential determining ions*, while the reduction in the potential away from the solid surface is determined by the properties of the solution such as strength of the solution and type of ions in the solution. In the so-called *Stern layer*, the solvated ions are immobile, and thus, the movement of ions and flow of solvent can only take place at a certain distance away from the Stern layer. This is the so-called *shear layer*.

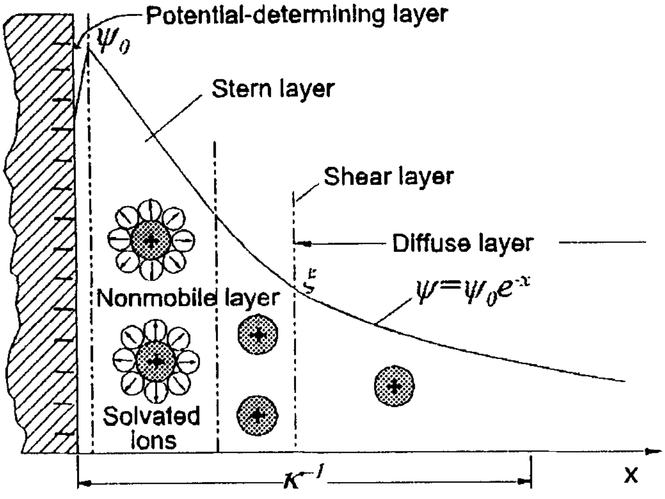

FIG. 3.
Model of electrical double layer[10,14].

The potential at this distance is known as the *Zeta potential* z, and the effective thickness of the double layer is defined as k^{-1}, which is the same as the *Debye length.*

According to the above model, the electrical double layer on the wall of a capillary will interfere with the ionic clouds in the solution, and thus affect the movement velocity of both the ions and the fluid. Therefore, in a porous material, the ionic diffusion will also be influenced by the effect of the double layer. The smaller the capillary is compared to the Debye length, the bigger is the effect of the double layer and the smaller becomes the drift velocity of the ions. Also, the larger the Debye length is for a given capillary, the slower do the ions move. Fig. 4 shows the distribution of the fluid velocity inside a capillary. While Fig. 5 shows the influence of capillary size relative to the thickness of the double layer on fluid velocity, from which it can be seen that on the surface of a capillary wall where $r_x = r_0$, the fluid almost becomes immobile due to the effect of the double layer.

The electrical double layer on the surface of charged species also builds up a repulsion potential barrier as shown in Figs. 6 and 7. For a given solid, the attraction potential due to Van der Waal's forces is constant. Therefore, the potential barrier is primarily determined by the

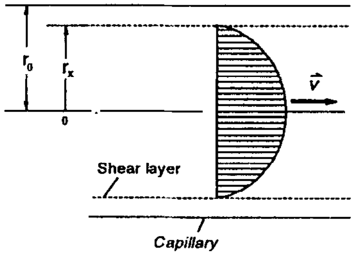

FIG. 4.
Velocity distribution of flow in a capillary[14].

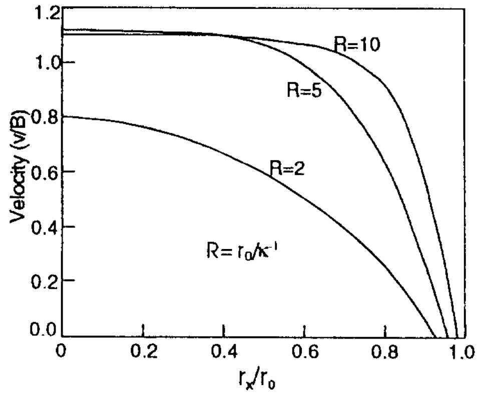

FIG. 5.
Influence of capillary size on the velocity distribution of flow in a capillary$^{(14)}$.

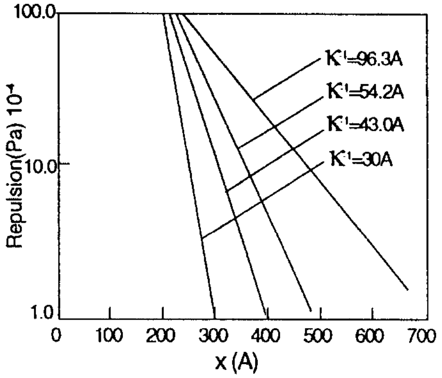

FIG. 6.
Repulsion variation with the distance between the charged plates$^{(15)}$.

properties of the electrolytic solution and the thickness of the double layer. According to the colloid stability or DLVO theory$^{(14-15)}$, the diffusing force must be large enough to overcome the potential barrier in order for the species to move closer to each other. Fig. 7 shows that in a weak solution, the repulsion is overwhelming, while as the strength of the solution increases, the repulsion potential decreases. When the solution becomes very strong, the repulsion will disappear and in turn, the attraction potential becomes dominant.

When the ionic clouds have the same sign as that of the electrical double layer on the capillary wall, the increased repulsion barrier may prevent the chloride ions from entering the capillary. For a given capillary size, therefore, it appears to be a minimum concentration necessary for the ions to diffuse into the concrete.

For a given ionic concentration, it appears that the ions can only enter capillaries above a certain size. One implication of this would be that the diffusing rate of chlorides into concrete

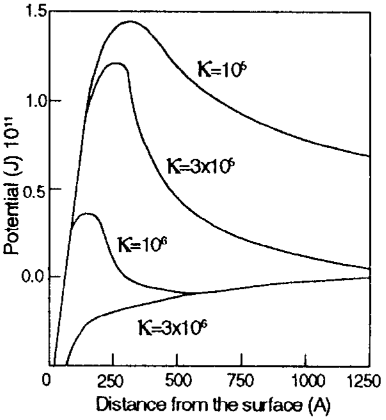

FIG. 7.
Variation of potential on a charged particle with strength of solution$^{(15)}$.

from a solution based on $CaCl_2$ should be higher than that of NaCl even though the chloride ion concentration is kept the same. Also, if the capillaries or the pore sizes become small enough, it is less likely for the ions to be able to diffuse into the concrete, even at a high concentration, because the thickness of the double layer and the ionic cloud cannot be further compressed. This is probably one of the reasons why both condensed silica fume and blast furnace granulated slag so effectively increase the resistance to chloride diffusion(1,16-17), since these materials so effectively reduce the pore sizes. This is probably one of the reasons also why the transport behavior of chloride ions in high performance concrete that is characterized by a very fine pore system, deviates so much from Fick's law of diffusion(18).

However, if most of the pores in a porous material are large enough compared to that of the ion radii, the number of chloride ions passing through a cross-section through a unit length of time should roughly be proportional to the porosity (p) but inversely proportional to the square of the thickness of the ionic cloud ($\tau = \kappa^{-1}$):

$$J \propto p/\tau^2 \propto \kappa^2 p \tag{18}$$

Chloride Diffusion in Concrete

In a solid-electrolytic solution system such as concrete, both the properties of the chloride containing solution and the interaction between the solution and the solid may affect the chloride diffusion process in the following way:

(1) Reduction in chemical potential and diffusing driving force arising from the effect of ionic interaction.
(2) Retardation of drift velocity of the chlorides from the lagging motion of the cations.
(3) Effect on the chloride drift from the interaction between the electrical double layer on the solid surface and the ionic clouds surrounding the diffusing chloride ions.

Based on these mechanisms, it is possible to estimate the relative values of a chloride diffusivity obtained from different types of salt solution. For some typical salt solutions, a ranking can be obtained as follows:

$$d_{LiCl} < D_{NaCl} < D_{KCl} < D_{CaCl_2}$$

Such a ranking is consistent with most experimental results reported in the literature (3-5).

It should be noted, however, that the above estimation is based on very dilute solutions compared to that typically used for testing of chloride diffusivity in concrete. For more concentrated solutions, the ionic clouds loose their smoothness and hence, the Debye-Hückel theory is no longer valid. For such solutions, the "quasi-lattice" theory has been introduced(10), but so far, it has not been possible to make any practical application of this theory.

In concrete, the pore solution also contains a variety of other ions, which will make the interference with the chloride ions even more complicated. The chemical binding of penetrating chlorides will also effectively reduce the amount of free chlorides and thus slow down the diffusion process(19-20). Therefore, the diffusion behavior of chloride ions in concrete is the result of several complex and complicated transport mechanisms.

Conclusions

In the present paper, an analysis of the diffusion behavior of chloride ions in concrete is presented, from which the following conclusions appear to be warranted:

(1) The diffusion behavior of chloride ions in concrete is a more complex and complicated transport process than what can be described by Fick's law of diffusion.
(2) In addition to the chemical binding, the effects of ionic interaction, lagging motion of cations and formation of electrical double layer on the solid surface are all playing an important role in the diffusion behavior of the chloride ions.
(3) A chloride diffusivity obtained from exposure to a salt solution does not only depend no the intrinsic properties of the concrete, but also on the physical-chemical properties of the external salt solution.

Acknowledgment

The present work that is part of a more comprehensive research program on long term performance and operation of concrete structure in the marine environment, is currently going on at the Division of Building Materials at NTNU in Trondheim. The authors would like to acknowledge the financial support received from the Norwegian Coast Directorate.

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