7 DIFFUSION BEHAVIOR OF CHLORIDE IONS IN CONCRETE

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ABSTRACT

Based on fundamental electrochemical theories, 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, it is shown that the effect of ionic interaction may significantly reduce the chemical potential and thus the driving force of the diffusing species. Because of the different drift velocities of the cations and the chloride ions in the solution, the lagging motion of the ionic atmosphere surrounding the chloride ions will also retard the drift velocity of the chlorides. In addition, the electrical double layer formed on the solid surface of the porous material may significantly interfere with the transport of chloride ions. As a result, the diffusion behavior of the chloride ions in concrete will not follow Fick's law very well, and particularly not in high density concrete with a fine pore structure. Also, the diffusion coefficients from concentrated chloride salt solutions will not be constant. An equation for describing the diffusion behavior of ionic species in concrete is introduced, where both type and concentration of electrolyte as well as porosity of the material are taken into account. Based on this equation, some estimates of chloride diffusivity in concrete exposed to different chloride salt solutions compared to that experimentally observed are presented. These results indicate that the new equation may provide a certain basis for a more general evaluation of chloride diffusivity in concrete.

INTRODUCTION

Transport of chloride ions inside a moist concrete is normally assumed to be governed by a diffusion process which obeys Fick's law of diffusion\(^1\). During testing for 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\(^2\). Also, a change in type of external salt solution, even though the chloride concentration is the same, may significantly affect the rate of chloride ingress into the concrete\(^3\).

From an electrochemical point of view, 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 characteristics of the external salt solution. Normally, all these effects are ignored. Thus, when concrete is exposed to a concentrated electrolytic solution such as seawater or that typically used in laboratory experiments, the effect of ionic interaction is so strong that it may significantly affect the diffusion behavior. 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
for migration testing of chloride diffusivity in concrete. In the present paper, a more
complete analysis of the electrochemical effects in ionic aqueous solutions which may affect
the diffusion behavior of chloride ions in concrete, is presented.

REDUCTION IN CHEMICAL POTENTIAL

For a non-interacting system, the chemical potential of a species $i$ is given by

$$\mu_i = \mu_i^0 + RT\ln c_i$$

where $\mu_i^0$ = chemical potential of the solute $i$ in the standard state
$c_i$ = concentration of species $i$
$R$ = gas constant
$T$ = absolute temperature

Since the driving force of a diffusing species comes from the gradient of its chemical
potential, the steady-state diffusing flux $J$ can be expressed as:

$$J \propto \frac{dc_i}{dx}$$

where $B$ is the proportionality. Thus, the diffusion coefficient $D$ is a constant:

$$D = BRT$$

and Eq. (2) becomes Fick's first law.

For an electrolytic solution, however, a condition exists, where

$$\mu_i - \mu_i^0 \neq RT\ln c_i$$

By introducing a correction factor $f_i$, the so-called activity coefficient, Eq. (1) becomes

$$\mu_i = \mu_i^0 + RT\ln c_i + RT\ln f_i$$

where, $c_i f_i = a_i$ is called the activity of the species $i$. For an infinite dilute solution, $f_i = 1$, and
its activity can be considered to be equal to its concentration.

Then, the flux becomes:

$$54$$

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Thus, the diffusion coefficient $D$ can be expressed as:

$$D = BRT \left(1 + \frac{d \ln f_i}{d \ln c_i} \right)$$  \hspace{1cm} (7)$$

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

According to the Debye-Hückel theory or the so-called ionic cloud theory\(^{12-13}\), the decrease in chemical potential $\Delta \mu_{i,j}$ in the electrolytic system is ascribed to ionic interaction, and its calculation is given as follows\(^{12,14}.

$$\ln f_i = -\frac{N_A (z_i e_0)^2}{2 R T \epsilon} \left( \frac{\kappa}{1 + a \kappa} \right) = -A \frac{1}{\epsilon} \frac{\kappa}{1 + a \kappa}$$  \hspace{1cm} (8a)$$

where

- $N_A = \text{Avogadro constant}$
- $R = \text{gas constant}$
- $\epsilon = \text{dielectric constant of the solution}$
- $e_0 = \text{charge of proton (electron)}$
- $z_i = \text{ionic valence}$
- $\kappa^{-1} = \text{Debye length (thickness of ionic cloud)}$
- $a = \text{average hydraulic radius of ions}$

and

$$A = \frac{N_A (z_i e_0)^2}{2 R T}$$  \hspace{1cm} (8b)$$

The calculation of $\kappa$ is also given by the Debye-Hückel theory\(^{12}.

$$\kappa = \left( \frac{8 \pi N_A e_0^2}{1000 \epsilon k T} \right)^{1/2} I^{1/2} = B \cdot I^{1/2}$$  \hspace{1cm} (9a)$$

$$B = \left( \frac{8 \pi N_A e_0^2}{1000 \epsilon k T} \right)^{1/2} = B_0 \epsilon^{-1/2}$$  \hspace{1cm} (9b)$$

where $k$ is the Boltzmann constant and $I$ is the ionic strength.

As can be seen from Eq. (9), the Debye length is controlled by several parameters of the solution such as type of electrolyte, concentration of solution and ionic valence $z_i$. In Fig.1,
the relationship between the Debye length and the concentration of the electrolyte has been plotted, from which it can be seen that the Debye length for a 1:1 type of electrolyte is always larger than that of a 1:2 type of electrolyte at any salt concentration.

![Graph showing relationship between Debye length and concentration of electrolyte.](image)

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

In addition, the dielectric constant $\varepsilon$ 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:

$$\varepsilon = \varepsilon_0 - \beta c$$  \hspace{1cm} (10)

From the above, it can be seen that the activity coefficient of a species depends on several parameters through $\kappa$ and $\varepsilon$, which reflect the effect of ionic interaction in the system. When $|d\ln f/d\ln c_i| << 1$ for a given solution, the diffusion coefficient $D$ can be considered to be a constant, and hence Fick’s law becomes a good approximation.

By considering chloride ions being the diffusing species and differentiating Eq. (8) with respect to its concentration $c_i$ combined with Eqs. (9) through (10), a change in the chemical potential of the ionic species can be obtained.

Fig. 2 shows the plot of change in chemical potential vs. concentration of chloride salt.

From Fig. 2 it can be seen that in chloride solutions, even at a very low concentration, the effect of ionic interaction becomes strong enough to significantly reduce the chemical potential of the ionic species. Thus, for chloride concentrations of up to 0.1 and 0.5 M, the decrease in chemical potential is up to about 10 and 16%, respectively. Therefore, for most chloride concentrations practically used for testing of chloride diffusivity, the apparent diffusion coefficient $D$ is not a constant.
RETARDATION OF DRIFT VELOCITY

The steady-drift of a diffusing species in a non-interacting viscous system can be approximately described by Stock’s relationship\(^{(11-12)}\)

\[
F_d = 6\pi\eta r \nu_d
\]

where \(\nu_d\) is the steady-drift velocity of the diffusing species, \(\eta\) is the viscosity of the solvent, and \(r\) is the radius of the diffusing species.

In electrolytic aqueous solutions, however, the anions and the cations usually move at different velocities due to their different mobilities. This corresponds to the motion of the whole ionic cloud relative to the central ions as shown in Fig. 3, where the relative motion of the ionic cloud is balanced by the Stock’s viscous force:

\[
F' = 6\pi\eta r \kappa^{-1} \nu'
\]

Here, \(\nu' = \nu_+ - \nu_0\) is the difference between the velocity of chloride ions (\(\nu_0 = \nu_0\)) and that of the cations in the solution (\(\nu_+\)), and \(\kappa^{-1}\) is the thickness of the ionic cloud.

Therefore, in a steady-state drift, the driving force \(F_d\) is balanced by both \(F'\) and \(F^0\):

\[
F_d = F^0 + F' = 6\pi\eta r (r + \kappa^{-1}(1 - \nu_+ / \nu_0))
\]
where, $F^0$ is the viscous resistance of the solvent to the chloride ions if both the anions and cations move with the same velocity. The values of $v_-$ and $v_+$ are unknown, but the ratio $v_+ / v_-$ can be assumed to be unchanged and estimated according to the "standard" mobility ($u^0_+$) or conductivity ($\lambda^0_+$) of the chloride ions and the cations by use of the following relationships:

\[ v_- = u_x F_d \]  \hspace{1cm} (14a)
\[ \lambda_- = u_x z_x F_d \]  \hspace{1cm} (14b)

From the Eqs. (18) and (19), a comparison of the diffusing rates of the chlorides from different electrolytic solutions with the same chemical driving force $F_d$ can be carried out.

**EFFECT OF ELECTRICAL DOUBLE LAYER**

In all solid-electrolytic solution systems, the formation of an electrical double layer on the solid surface is an important phenomena, a model of which is shown in Fig. 4. The surface potential $\psi_0$ is determined by the rigidly adsorbed ions, the *potential determining ions*, while the reduction in the potential along the direction away from the solid surface is determined by the properties of the solution such as strength of 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 outside the Stern layer. This is called the *shear layer*. The potential at this layer is known as the Zeta potential $\zeta$, and the effective thickness of the double layer is defined as $\kappa^{-1}$, 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 that of 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. 5 shows the distribution of the fluid velocity inside the capillary. while Fig. 6 shows the relationship between the fluid velocity and the capillary size relative to the thickness 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. 7 and 8. 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 properties of the electrolytic solution and the thickness of the double layer. According to the colloid stability theory or DLVO theory (15-16), the diffusing force must be large enough to overcome the potential barrier in order for the species to move closer to each other. Fig. 8 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, it appears, therefore, to be a minimum concentration necessary for the ions to be able to diffuse in. Also, 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 from a solution based on CaCl₂ should be higher than that of NaCl with the same chloride source concentration. This is actually being experimentally observed⁵⁶. Also, if the capillaries or the pore sizes become too small, 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 fume⁶ and blast furnace granulated slag¹⁷ so effectively increase the resistance of concrete to chloride diffusion. This is probably one of the reasons also why the transport behavior of chloride ions in high density concrete with a fine pore structure does not follow Fick’s law of diffusion¹⁸.

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 be roughly proportional to the porosity (p) but inversely proportional to the square of the thickness of the ionic cloud (τ=κ¹):

$$J \propto \frac{p}{\tau^2} \propto \kappa^2 p$$  \hspace{1cm} (15)

**CHLORIDE DIFFUSION IN CONCRETE**

If the diffusion system is considered to be a porous solid with continuous pores filled up with a chloride containing electrolytic solution, both the properties of the 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 ionic cloud surrounding the chloride ions.
3. Effect on the chloride drift due to the interaction between the electrical double layer and the ionic clouds surrounding the diffusing chloride ions.

Based on the above effects discussed in the present paper, the following equation has been developed for describing the diffusion behavior of ionic species in concrete:

$$J = -BT \frac{dc_i}{dx} \frac{1+dlnf/dn_c_i}{6\pi \eta[r+\kappa^{-1}(1-v/v_j)]} \kappa^2 p$$  \hspace{1cm} (16)

In order to apply this equation, a number of parameters, functions, assumptions and simplifications have to be made. However, on the basis of this equation, a rough comparison of the diffusion rate and apparent diffusivity of chloride from different electrolytic solutions.
can be made. Thus, for solutions based on NaCl and CaCl₂, the following parameters can be selected:

\[
v_{Ca^+}/v_{Cl} = \lambda_{Ca^+}^{0}/\lambda_{Cl}^{0} = 59.50/76.34 = 0.7794
\]

\[
v_{Na^+}/v_{Cl} = \lambda_{Na^+}^{0}/\lambda_{Cl}^{0} = 50.11/76.34 = 0.6564
\]

and \(C\) calculated on the basis of Eq. (9). The average hydraulic radius of the ions \(r\) can be selected to be \(4\AA^{14}\), while \(1+\text{dln}f/\text{dln}c\) can be either calculated or estimated from Fig. 2.

In Table 1, a comparison between measured\(^6\) and estimated values of chloride diffusivity obtained from different salt solutions is shown. In these experiments, all the solutions had the same chloride source concentration, and the diffusion coefficients were calculated on the basis of Fick's second law. As can be seen from the table, the theoretical estimates are quite consistent with the experimental results. Therefore, Eq. (16) may provide a certain basis for a more general evaluation of chloride diffusivity in concrete.

When the concentration of an ionic solution become so high that the thickness of the ionic clouds is compressed to the magnitude of the average hydraulic radius of the ions, the ion clouds loose their smoothness and hence, the Debye-Hückel theory is no longer valid. For such a case, the "quasi-lattice" theory has been introduced\(^{12}\), but so far, it has not been possible to make any practical application of this theory.

In reality, the process of chloride ingress into concrete is more complex and complicated than that discussed in the present paper. The specific environmental conditions always play an important role. Also, the ability of the cement paste both to physically and chemically bind chlorides is very important\(^{19-20}\). While the physical bound chlorides may be considered being part of the electrical double layer, the chemical binding of penetrating chlorides may effectively reduce the amount of free chlorides in the pore solution and thus slow down the diffusion process. In order also to take this effect into consideration, further studies are needed.

Table 1. Comparison between measured and estimated values of chloride diffusion coefficients.

<table>
<thead>
<tr>
<th>Chloride source solution (0.5 N)</th>
<th>Diffusion coefficient (D) (cm²/s) (\times 10^{-8})</th>
<th>Ratio of (D_{II}/D_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Estimated</td>
</tr>
<tr>
<td>LiCl</td>
<td>3.13</td>
<td>5.63</td>
</tr>
<tr>
<td><strong>NaCl</strong></td>
<td>6.25</td>
<td>6.25</td>
</tr>
<tr>
<td>KCl</td>
<td>6.73</td>
<td>8.19</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>10.38</td>
<td>11.00</td>
</tr>
</tbody>
</table>

* Reference

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CONCLUSIONS

Based on fundamental electrochemical theories, an analysis of the diffusion behavior of chloride ions in concrete has been carried out, from which the following conclusions appear to be warranted:

(1) The diffusion of chloride ions in concrete exposed to concentrated salt solutions is not a Fick type of diffusion, which is valid only for non-interaction systems.

(2) The diffusion coefficients obtained from concrete exposed to concentrated chloride solutions not only depend on the material parameters but also on concentration and type of chloride solution.

(3) The equation introduced in the present paper (Eq. 21), which describes the diffusion behavior of ionic species in concrete, may provide a certain basis for a general evaluation of chloride diffusivity in concrete.

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