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A novel method for describing chloride ion transport due to an electrical gradient in concrete: Part 1. Theoretical description

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Abstract

This paper is the first of two reporting the development of a novel method for describing the transport of chloride ions in concrete under an electrical gradient. In this part, the theory is described and developed. In the second paper, experimental evidence to support the proposed theory is provided. This new theory is designed to correct some deficiencies of the current state of the art. Namely, it considers the effect of concrete being a porous media rather than considering concrete as an aqueous solution as is done with the standard laws; for example, the Nernst–Planck equation.

Keywords: Concrete; Transport properties; Pore size distribution; Ionic migration

1. Introduction

The ability of concrete to resist the penetration of chloride ions is often a key component in determining the durability of marine or deicing salt-exposed concrete structures. As such, the transport of chloride ions has been extensively studied, including the development of test methods to rapidly assess the ability of concrete to resist the penetration of chloride ions. As the rate of chloride ion penetration due to diffusion alone is slow, techniques are used to accelerate this process for evaluating concrete. The most common method is through the application of an electrical potential. While there has been success relating the diffusion coefficient in concrete to parameters developed from these tests [1–3], there have been questions regarding the completeness of the current theory describing the transport process. In Part 1 of this series of papers, the current theory used to describe the movement of ions under an electrical gradient is evaluated and its weaknesses discussed. This leads to the description of an alternative theory. In Part 2, experimental evidence is obtained for this theory [4].

2. Description of current theory

When an electrical field is applied, movement of chloride ions is due to two driving forces, diffusion, and migration. It can be stated that [1]:

$$J_T = J_M + J_D \tag{1}$$

where J_T is the total flux, J_M is the flux due to migration, and J_D is the flux due to diffusion. Applying the results for solutions, the flux due to diffusion can be determine from Fick's first law [1]:

$$J_D = -D\frac{\partial C}{\partial x} \tag{2}$$

where D is the chloride diffusion coefficient of concrete, C is the chloride concentration, and x is a position variable. To determine the flux due to migration, again applying the results for solutions, the Nernst–Planck Relation is used to derive the equation [1]:

$$J_M = \frac{zFD}{RT}C\frac{U}{L} \tag{3}$$

where z is the valence of chloride (Eq. (1)), F is Faraday's constant (9.648×10^4 J/Vmol), U is the potential difference

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across the sample, R is the universal gas constant (8.314 J/molK), T is the temperature, and L is the length of the sample. Substituting Eqs. (2) and (3) into Eq. (1) results in the differential equation:

$$J = -D\frac{\partial C}{\partial x} + \frac{zFD}{RT}C\frac{U}{L} \tag{4}$$

Solving for the nonsteady state, constant surface concentration, infinite thickness boundary conditions result in the numerical solution [1]:

$$C(x,t) = \frac{C_0}{2}\left(e^{ax}\mathrm{erfc}\left(\frac{x+aDt}{2\sqrt{Dt}}\right) + \mathrm{erfc}\left(\frac{x-aDt}{2\sqrt{Dt}}\right)\right) \tag{5}$$

where C_0 is the surface concentration, t is the time, a = zFU/RTL, and erfc is the complementary error function.

There are a number of influences that this development does not attempt to address; for example, chloride binding and the influence of other ions. Other models based upon the Nernst–Planck equation have been proposed to account for the influence of other ions that may be present in the pore solution [5–9], but these greatly increase the complexity of the model and require additional information that is not normally available. They also similarly suffer from the drawback that will be discussed.

There is an additional resistance to chloride ion movement—chloride binding. Once a chloride ion has been bound in the matrix, it is no longer free to move. It is only the free chloride ions in the pore solution that are moving. When the concrete chloride profile is determined, however, it is not the free chloride concentration that is established, but the total chloride concentration—both free and bound. As the chloride ions penetrate the concrete, some of the ions become bound, thus reducing the free chloride concentration that is available to penetrate the next portion of the concrete. This contributes a resistance to the transport of chloride ions that needs to be considered.

One approach to model the effect of binding would be to consider this effect explicitly. This would involve the establishing of binding isotherms over the range of chloride concentrations that would be experienced, determining whether equilibrium is maintained or whether the kinetics of the reactions need to be considered and then accounting for this in the model. This approach presents difficulties beyond the establishment of the necessary parameters that make it inappropriate. Realize that the amount of chloride bound depends upon the local chloride concentration in the individual pore of interest. However, the parameter that is under consideration is not this value but the global chloride ion concentration. The concentration in the pores will vary significantly from this value and will vary from pore to pore. The exact nature of this variation remains unknown but would be necessary to establish so as to establish the bound chloride ion concentration due to the nonlinear nature of the chloride binding isotherms.

The second approach would be to include the effect of binding implicitly. In this approach, the additional resistance caused by the binding would be included in the material parameters. This is similar to the current use of apparent diffusion coefficients, including the effect of binding versus the use of effective diffusion coefficients that do not. This implicit approach does have the disadvantage of only describing the total chloride ion concentration profile and not discriminating between the free and bound chlorides. Total chloride ion concentration, however, is the concentration normally determined experimentally. This approach is also commonly used in evaluating migration data and will continue to be used in this work. The effect of binding is included in the material parameters.

To illustrate the deficiency of the theory developed considering concrete as a form of aqueous solution, a chloride concentration profile of a sample after exposure to a fixed voltage with a fixed surface concentration is shown in Fig. 1. Also shown is the theoretical profile (Eq. (5)) with the diffusion coefficient based upon the toe of the curve and the equation developed by Tang [1]. It can be seen that the theoretical profile does a poor job predicting the experimental profile. The predicted transition between the regions of high and low concentration is much more abrupt than that determined experimentally. In addition, there is a predicted region of constant chloride concentration that is not present in the experimental profile. The experimental profile displays a gradual transition between the surface concentration and the background concentration. The predicted profile is not improved by using a more complicated model considering all the ions present in the pore water. The transition is still predicted as abrupt, as can be seen in Truc [5].

This discrepancy has been observed by previous workers, such as by Tang and Nilsson [10], Tang [1], and Truc [5]. Truc attributes this variation to the effect of integrat-

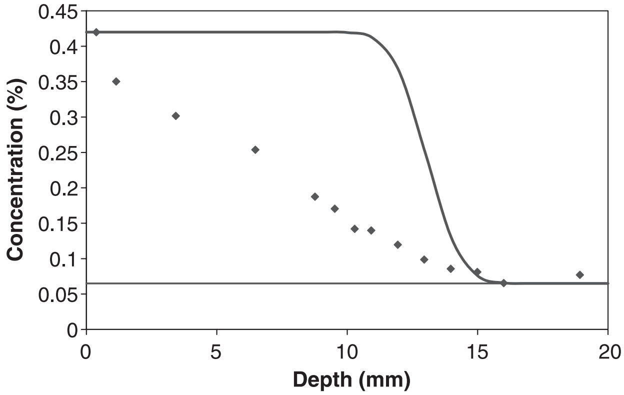


Fig. 1. Comparison of experimental profiles from Stanish et al. [12] and predicted profiles according to Tang [1].

ing the chloride concentration over the thickness of the ground layers. The results he reports do not, however, result in a profile with as gradual a transition as has been determined in Fig. 1 and are calculated with a layer thickness, while unreported, that appears to be greater than that used in this work. The greater the layer thickness, the greater the effects of the integration on the chloride profile. At this time, to the authors' knowledge, no other explanation for this discrepancy has been proposed.

3. Mechanisms omitted in previous solutions

Prior to this point, two fundamental relationships have been used almost exclusively—Fick's law to describe diffusion and the Nernst–Planck equation to describe migration. These relationships have been used with success in other fields, for example, chemical engineering, and it appears reasonable to apply these relationships to the problems presented here. In concrete, however, there is an important aspect that these relationships do not account for. While the transport of chloride ions in concrete is the movement of ions in a porous media, these equations were developed considering the movement of a low concentration of ions in a solution. If a model does not consider the effect of the solid matrix portion of the porous media on the transport of particles through the porous media correctly, it is likely that the model will be incapable of correctly predicting ion distributions and the evolution of concentration profiles in porous media.

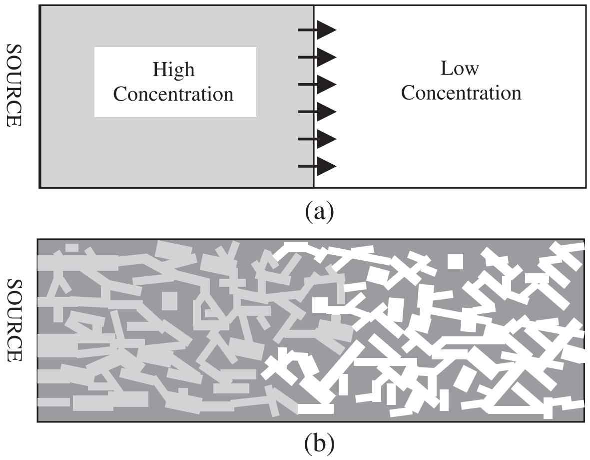
In solution, ions are free to move in any direction and are only impeded by the other molecules in solution, which are also moving. In a porous media, the ions are only free to travel through the liquid-filled pore space. The ions cannot travel through the solid pore walls. This means that while on a microscopic scale in a pore, these two laws are obeyed; they are not obeyed on a macroscopic scale, as illustrated in Fig. 2. Thus, it can be said that the pore structure places an additional resistance to ionic movement in concrete. However, this resistance to ionic movement is not constant for all ions in all pores. In some pores, the additional resistance will be rather low as the direction the ions tend to travel corresponds with the direction that the pore allows them to travel. In other pores, the resistance would be higher as the ions and pores are not heading in the same direction. The effect of this different resistance is to create a transition region in concentration, as indicated in Fig. 2. Thus, the application of either Fick's law or the Nernst–Planck Relationship without modification to the problem of transport in a porous media is omitting a significant effect.

4. An alternative approach

It is thus necessary to develop an approach that does not have the limitations of the advective dispersion equation just described. To do this, a more fundamental understanding of ionic transport needs to be developed.

4.1. Conceptualization of transport equations

In any transport situation, there are two things that must be considered. First, there is the impetus—the force that causes the movement to occur. In migration, this force is the electrical potential gradient; in permeation, the impetus is the pressure gradient; and in diffusion, the impetus is the concentration or activity gradient. In addition, there is some resistance to movement. This resistance is what prevents the rate of transport from accelerating indefinitely. Thus, the velocity at which transport occurs is the result of the balance between the resistance, generally due to the composition and pore structure of the materials and the impetus generally due to some external force. All transport



In a solution (a), the particles are free to travel in any direction. Thus they are able to travel uniformly from left to right. In a porous media (b), the movement of the ions is restricted and thus is more complicated. Thus, ions globally obey Fick's Law and the Nernst-Planck Equation in (a), but not in (b).

Fig. 2. Effect of pore structure on transport laws.

equations can be conceptualized as a specific case of the general equation:

$$v = \frac{1}{R} \times I \tag{6}$$

where v is the velocity of the particles, R is the resistance, and I is the impetus. As an alternative, the resistance could be replaced by its inverse called the penetrability, P. The general equation then becomes:

$$v = P \times I \tag{6a}$$

To illustrate this effect, let us consider some transport equations that have already been developed for solutions.

For migration, the Nernst–Planck equation applies:

$$v = \left(D\frac{zF}{RT}\right)\left(\frac{dU}{dx}\right) \tag{7}$$

In this case, the first bracket is the penetrability symbolized by the diffusion coefficient and the ionic valence as well as some constants. The second bracket is the impetus—the potential gradient.

For permeation, to calculate average velocity of flow ($\bar{v}$), D'Arcy's law applies:

$$\bar{v} = \left(\frac{k}{n}\right)\left(-\frac{dh}{dx}\right) \tag{8}$$

In this case, the penetrability (the first bracket) is the permeability coefficient (k) and the porosity (n), while the impetus (second bracket) is the hydraulic gradient [change in hydraulic head (h) with distance (x)].

For diffusion, Fick's law applies:

$$J = (D)\left(-\frac{dC}{dx}\right) \tag{9}$$

In this case, the penetrability is represented by the diffusion coefficient, while the impetus is the concentration gradient.

Of these equations, two (Nernst–Planck equation and Fick's law) were not developed for porous materials, and thus do not include the effect of the pore structure. The other equation (D'Arcy's law) is dealing with transport through a porous body but only purports to give the average velocity in the pores—the actual velocity in any one pore can widely differ. An additional consideration is necessary when dealing with transport through porous structures that has not yet been considered.

To develop this additional consideration, it needs to be realized that the effect of the pore structure is not to supply additional impetus, but to modify the penetrability that is experienced by the travelling particles. In other words, the penetrability is then made of two components:

$$P = P_{\mathrm{s}} \times P_{\mathrm{p}} \tag{10}$$

where P_{s} is the penetrability of the particles travelling through the solution and P_{p} is the modification to the penetrability caused by the pore structure. The penetrability of the solution has already been described by the existing equations, i.e., for migration, it is described by Eq. (7). To fully describe the situation when a porous media is involved, it is only thus necessary to determine the additional modification provided by the porous media, P_{p}.

Numerically, it is obvious that this factor must take on positive values that are less than or equal to one. A negative value would mean that the pore structure would cause the transport to reverse direction. While this may be possible in a single pore where the geometry forces the flow to reverse direction, this will not be the case on a global scale. A value of greater than one would mean that the inclusion of the effect of the pore structure would cause the transport to accelerate—to go faster than it otherwise would.

4.2. Relationship to dispersion

So how does this conception of transport aid in the description of the dispersion previously observed? A single porous media are made up of a collection of pores, each with their own separate characteristics. A single particle will travel down a single pore and thus experience a specific individual modification to its rate of transport causing it to travel at a specific average velocity. However, at any one time, there are a multitude of pores and a multitude of particles. Each particle would thus experience its own separate transport rate. Thus, the modification to penetrability provided by the pore structure, P_{p}, should be not a single value, but a function that leads to a distribution of velocities and thus a variation in concentration.

It is now necessary to predict the shape of this function. Consider the pore structure to be made up of a large number of individual pore bodies with dimensions on the order of micrometers. Each of these pore bodies will provide its own modification to the penetrability that the particles experience. The distribution of these modifications is unknown. However, any ion traveling through the concrete will have to pass through many of these pore bodies, and the average modification to penetrability it has experienced will be a product of the individual modifications of the separate pore bodies. Using the central limit theorem, which states that the product of a large number of independent factors will tend to the lognormal distribution [11], it can be thus predicted that the resistance due to the pore structure would have the form:

$$P_{\mathrm{P}}(y) = \frac{1}{\sqrt{2\pi(\ln(\zeta))^2 \ln(y)}} \exp\left[-\frac{1}{2}\left(\frac{\ln(y) - \ln(\lambda)}{\ln(\zeta)}\right)^2\right] \tag{11}$$

where λ and ζ are constants, which can be interpreted as the mean and standard deviation of the natural logarithm of the distribution of the modification to the penetrability provided by the pore structure. This function provides information on the proportion of the particles travelling through the porous media that experience a specific modification to its penetrability. The modification to the penetrability is the input parameter, y, and the proportion of the ions that experience this modification is the value of the function, P_p, at this input. A typical distribution of the modifications to the penetrability is shown in Fig. 3.

The dimensionless parameters, λ and ζ, that describe the shape of this penetrability modification function are a function of the pore structure. They will be controlled by the pore size, tortuosity, and connectivity of the pores. The overall penetrability of the matrix is described by the average penetrability of the shape function, λ. If the penetrability of the matrix is increased—either by increasing the pore size, decreasing the tortuosity of the pores, or increasing their connectivity—this will be reflected in an increase in the material parameter, λ. The other material parameter, ζ, represents the uniformity of the pore structure and its corresponding modification to penetrability. If the pore structure is more uniform, for example, with a lower range in pore sizes, this will be reflected by a reduction in this parameter.

The proposed function, $P_p(y)$, has the required properties. Regardless of the material parameters, the value of $P_p(y)$ for all negative values of y is zero. In other words, none of the particles experience a negative modification factor, as is required. In addition, while the function $P_p(y)$ can take on positive values for modification factors (y) greater than one depending upon the values of the mean, λ, and deviation, ζ, this is not true for all of these values. The typical values encountered for migration in concrete, as will be seen in Part 2 [4], produce values of effectively zero (on the order of 10^{-7}) for the proportion of particles that experience a modification factor greater than one. Another important property of the proposed function is that the sum of $P_p(y)$ for all values of y is one. That is, expressed mathematically,

$$\int_{-\infty}^{\infty} P_p(y)dy = 1 \tag{12}$$

This is necessary to obey conservation of mass.

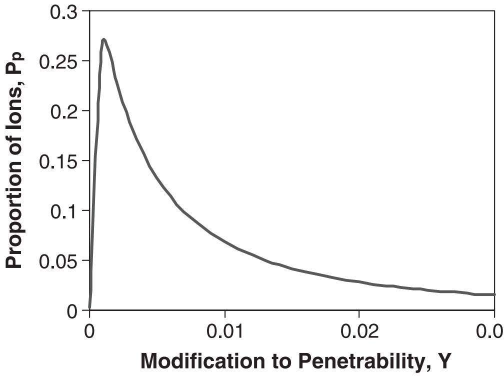


Fig. 3. Typical distribution of modification values.

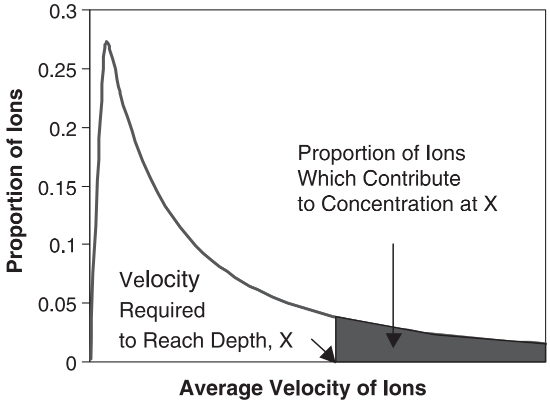


Fig. 4. Proportion of ions that contribute to the concentration at a depth, X, with a constant source concentration.

5. Summary of proposed model

Based upon the preceding discussion, a mathematical model can now be described. To establish a concentration profile, realize that with a constant source concentration, the concentration of ions at any depth at a given time is a function of the number of ions that have a sufficient velocity to travel that distance or farther. The particles that travel further starting from the source concentration at Time 0 represent particles that start at a later time and thus have only reached the depth of point of interest. Since there is a constant source concentration under consideration, these "late-starting" ions will always be present. This is illustrated in Fig. 4. To determine this proportion, the distance needs to be normalized by the distance an ion

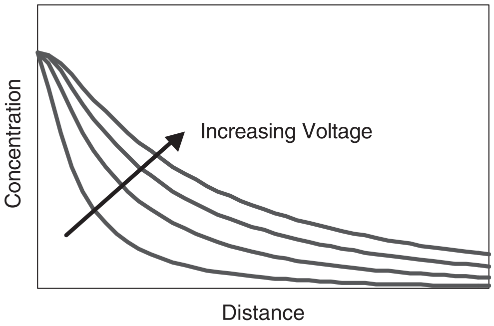


Fig. 5. Effect of altering test voltage.

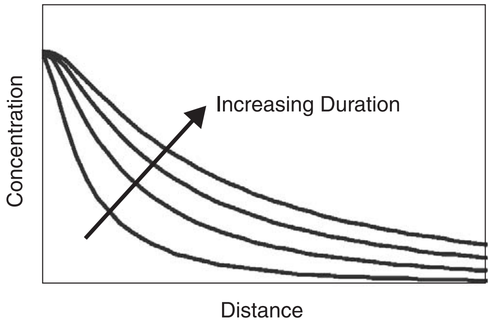


Fig. 6. Effect of altering test duration.

would travel in free solution to determine the normalized depth (y):

$$y = \frac{x}{\left(\frac{zFUDt}{RTL}\right)} \tag{13}$$

where x is the depth of the point of interest, D is the diffusion coefficient of the ion in free solution (a known value of 2.032×10^{-9} m^2/s), and the remainder as previously defined. This normalized distance, y, is thus the minimum modification factor that can be experienced by the ions and still reach that point. Now the portion of ions with a modification factor greater than this can be described by:

$$F(y, \lambda, \zeta) = \int_y^\infty P_\mathrm{p}(y)$$

$$F(y, \lambda, \zeta) = 1 - \int_0^y \left(\frac{1}{\sqrt{2\pi(\ln(\zeta))^2 \ln(u)}} \times \exp\left[-\frac{1}{2} \left(\frac{\ln(u) - \ln(\lambda)}{\ln(\zeta)} \right)^2 \right] \right) du \tag{14}$$

where $P_\mathrm{p}(y)$ is the distribution of modification factors (Eq. (11), λ and ζ represent the mean value and the standard deviation of the distribution of the penetrability of the pore structure, and y is the normalized depth. The function $F(y,\lambda,\zeta)$ then gives the proportion of the ions that have been able to reach the depth for the given voltage and duration used to calculate the y for that specific concrete as characterized by the λ and ζ. The additional concentration, above background, at that depth will thus be the product of this value and the surface concentration. Thus, the equation for the chloride concentration profile with a constant surface concentration can be derived, including background concentration, C_i:

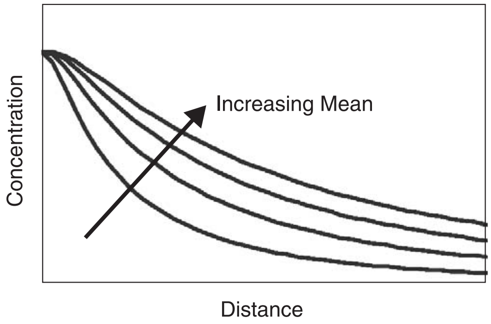


Fig. 7. Effect of altering mean in Eq. (15).

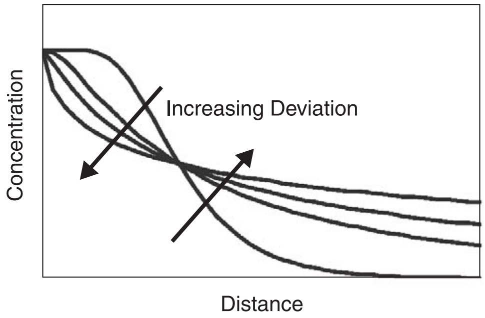


Fig. 8. Effect of altering deviation in Eq. (15).

$$C = C_0[F(y, \lambda, \zeta)] + C_i \tag{15}$$

The surface concentration, C_0, can be calculated as the product of the porosity and the solution concentration. In this case, it is the free surface concentration and does not include the contribution of the background chloride values.

5.1. Significance of parameters

To investigate the influence of varying the parameters present in the above equations, Figs. 5–8 were constructed. Each figure schematically illustrates the effect of varying the single parameter indicated.

Increasing the applied voltage or the testing duration increases the distance that the ions travel or the concentration at a specific point (Figs. 5 and 6). This is the desired outcome and agrees with previous experimental evidence [12]. Increasing the mean value of the lognormal distribution of the penetrabilities (Eq. (15)) similarly increases the distance the ions travel or the concentration at a specific point (Fig. 7). This is because the mean of the distribution represents the average penetrability of the pore structure. Increasing the standard deviation of the lognormal distribution of the penetrabilities (Eq. (15)) causes a “flattening” of the concentration profile (Fig. 8). A low value of the deviation causes an abrupt transition from high concentration values to low values. A high value of deviation causes a more gradual transition.

6. Conclusion

In this paper, it is shown that the existing models for the migration of chloride ions in concrete are deficient, and a new approach for describing the transport of chloride ions under an electrical potential gradient has been developed. It considers that the ions are travelling not through a dilute solution but through a porous matrix. The importance of this is suggested by the chloride concentration profiles that have been found experimentally. The variation in resistance caused by the pore structure is considered, and a lognormal distribution is proposed to model the resulting variation in penetrabilities. This results in two material parameters—the average value of penetrability and its variation. In the second part of this series, experimental evidence is shown for the validity of this approach [4].

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