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APPLICATION OF DANCKWERTS' SOLUTION TO SIMULTANEOUS DIFFUSION AND CHEMICAL REACTION IN CONCRETE

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ABSTRACT

A methodology is presented for the determination of chloride diffusivities when there is simultaneous chloride diffusion and reaction. The methodology does not expressly incorporate a choloride binding mechanism. The chloride diffusivities are comparable to those calculated with the Langmuir binding isotherm.

Introduction

Chloride in concrete is present either as free or bound chloride. Chloride is immobilized in the concrete by a combination of reaction with C_3A and C_4AF, and adsorption primarily into the C-S-H gel (1). The exact relationship between immobilized or bound chloride and free chloride is complicated. Pereira and Hegedus (2) and Page and co-workers (3, 4) used the Langmuir isotherm to describe the relationship between bound and free chloride. Recently, Tang and Nilsson (5) reported that the relationship between bound and free chloride can best be described by a combination of the Freundlich and Langmuir binding isotherms. Therefore, chloride diffusion equations involving free chloride concentration and the relationship between the bound and free chloride are mathematically complex. We present in this note, a mathematical solution to the problem of chloride diffusion into concrete with simultaneous reaction which does not require an express relationship between the free and bound chloride.

Model

Consider that all the processes which bind chloride into the concrete can be represented by a pseudo first-order reaction, and that the rate of this reaction is solely proportional to the free chloride concentration. Further, Fick's second law for unsteady state diffusion is valid for the diffusion of unreacted chloride through the concrete. Finally, the concrete has a plane surface and is of infinite depth. The initial chloride concentration in the concrete is uniformly equal to zero.

Let C_o represent the chloride concentration at the surface ($x = 0$), C is chloride concentration at some distance x below the surface, t is the time, and k is the rate constant for the pseudo first-order reaction. Now, consider an element of volume of unit cross-sectional area between two planes x and (x + dx). The following changes in chloride content occur in time dt,

$$\text{Chloride diffusion in:} \qquad -D\,\frac{\partial C}{\partial x}\,dt \tag{1}$$

$$\text{Chloride diffusion out:} \qquad -\left[-D\,dt\left(\frac{\partial C}{\partial x} + \frac{\partial^2 C}{\partial x^2}\,dx\right)\right] \tag{2}$$

$$\text{Chloride reaction:} \qquad -kCdt \cdot dx \tag{3}$$

$$\text{Net chloride increase:} \qquad \left(D\,\frac{\partial^2 C}{\partial x^2} - kC\right) dt \cdot dx \tag{4}$$

Eq. (4) is equal to the net chloride increase dC.dx. Therefore, Eq. (4) can be written as,

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} - kC$$

The following boundary conditions apply to the problem,

$$C = C_o,\ x = 0,\ t > 0$$
$$C = 0,\ x > 0,\ t = 0$$
$$C = 0,\ x = \infty,\ t > 0$$

Subject to the boundary conditions, Danckwerts' solution (6) to Eq. (5) is,

$$\frac{C}{C_o} = \frac{1}{2}\exp\left(-x\sqrt{\frac{k}{D}}\right) \cdot \operatorname{erfc}\left[\frac{x}{\sqrt{4Dt}} - \sqrt{kt}\right] + \frac{1}{2}\exp\left(x\sqrt{\frac{k}{D}}\right) \cdot \operatorname{erfc}\left[\frac{x}{\sqrt{4Dt}} + \sqrt{kt}\right] \tag{6}$$

where erfc is the statistical complimentary error function. The rate of reaction of chloride per unit of exposed concrete surface area is,

$$R_{\text{reaction}} = -D\left(\frac{\partial C}{\partial x}\right)_{x=0} = C_o\sqrt{Dk}\left[\operatorname{erf}\sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}}\right] \tag{7}$$

where erf is the statistical error function. The total chloride immobilized in time t is given by,

$$C_{\text{total}} = C_o\sqrt{\frac{D}{k}}\left[\left(kt + \frac{1}{2}\right)\operatorname{erf}\sqrt{kt} + \sqrt{\frac{kt}{\pi}}\,e^{-kt}\right] \tag{8}$$

For very long exposure times, Eqs. (6)–(8) reduces respectively to,

$$\frac{C}{C_o} \approx \exp\left(-x\sqrt{\frac{k}{D}}\right) \tag{9}$$

$$R_{reaction} \approx C_0\sqrt{Dk} \tag{10}$$

$$C_{total} \approx C_0\sqrt{Dk}\left(t + \frac{1}{k}\right) \tag{11}$$

When, kt = 0, Eqs. (6)–(8) reduces to the well-known equations for diffusion without reaction.

Experimental data to test the model are sparse because total chloride not the free chloride concentrations are usually measured. Furthermore, numerical regression techniques are statistically reliable only when there are a sufficient number of data points. Data from Page and co-workers (3, 4) has been used to test the model. The experimental data were fitted to Eq. (6) using the Levenberg-Marquardt algorithm (7). The experimental data and the model approximation are given in Figures 1 and 2. Values for D and k were determined by minimizing the chi-squared values. They are summarized in Table 1 together with chloride diffusivities determined assuming a Langmuir binding isotherm as reported by Page and co-workers (3, 4).

It can be seen from Figures 1 and 2 that Eq. (6) has a reasonable fit to the experimental data. The fit is considerably improved for the longer exposure time. The chloride diffusivities calculated with Eq. (6) are the same order of magnitude as diffusivities calculated using a model incorporating the Langmuir binding isotherm reported previously (3, 4). The very small values for k indicate that the binding of chloride is a fast process. The rate of chloride reaction per unit of exposed concrete can be calculated with Eq. (7). The values were 2.8 × 10^{-10} *moles* $cm^{-2}s^{-1}$ and 1.4 × 10^{-12} *moles* $cm^{-2}s^{-1}$, respectively for the data of references (3) and (4).

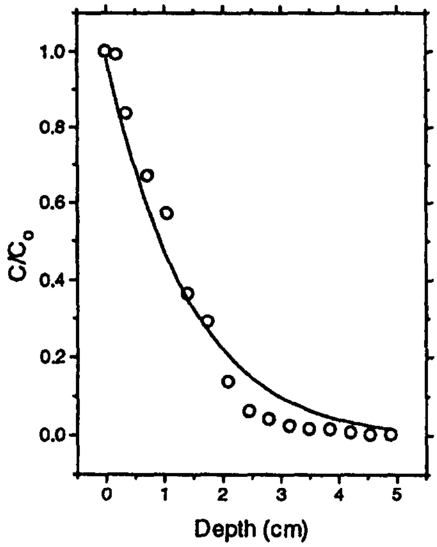

FIG. 1.
Data from Reference (3). Eq. (6) represented by solid line.

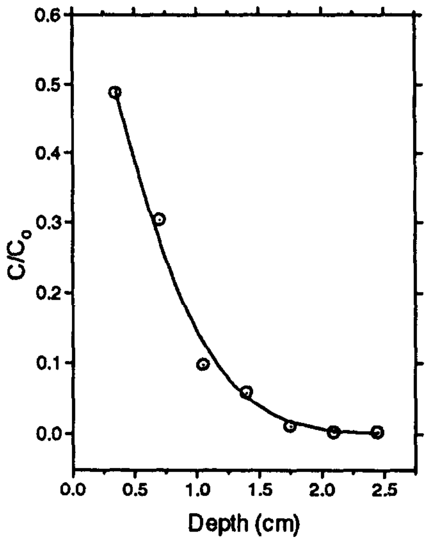

FIG. 2.
Data from Reference (4). Eq. (6) represented by solid line.

TABLE 1
Model Parameters

	Time	Eq. [6]		D*
	(*days*)	D (*cm*^{2} *s*$^{-1}$)	k (*s*$^{-1}$)	(*cm*^{2} *s*$^{-1}$)
Reference (3)	100	3.95×10^{-7}	1.82×10^{-7}	1.40×10^{-7}
Reference (4)	225	1.55×10^{-8}	1.73×10^{-10}	3.93×10^{-8}

*Reported in Ref. (3, 4).

Conclusions

- The methodology presented in this paper calculates the chloride diffusivity when the exact nature of the binding of chloride in concrete is unknown.
- The diffusivity values are comparable to those incorporating the Langmuir binding isotherm.
- The rate of reaction of chloride and the total immobilized can be easily and readily determined.

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