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A COMPLEMENT TO THE DISCUSSION OF A. XU* AND S. CHANDRA* ABOUT THE PAPER "CALCULATION OF CHLORIDE COEFFICIENT DIFFUSION IN CONCRETE FROM IONIC MIGRATION MEASUREMENTS" BY C. ANDRADE**

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Xu and Chandra's remarks (1) about an article of Andrade on the accelerated diffusion of chlorides (2) have the merit of clearing different aspects of the work of Andrade. The main remark is the point (Eq.6) that deals with the theoretical calculation of the concentration profile of chloride in a concrete or mortar specimen, which is the object of the two articles (1) and (2).

The mathematical model of ion diffusion obtained by Xu and Chandra is relevant and welcome. However the solution proposed in transitory state and the one that derives in steady state (when $t \longrightarrow \infty$) seems to be incorrect. In order to propose an adequate solution, first it is necessary to redefine the problem.

Problem Description

A concrete or mortar specimen of thickness L separates two semi-infinite solutions (Figure 1). The solution "A" is to a concentration of chlorides $C_A = C_0$ (constant). The solution "B" does not contain $C_B = 0$. To accelerate the diffusion process, an electrical field is applied on opposite sides of the specimen.

The arrangement represented in the Figure 1 is according to boundary conditions imposed by Xu and Chandra (p. 377); namely:

$$t > 0 \left\{ C(0,t) = C_0,\ C(L,t) = 0 \right\}$$

The initial condition is:

$$t = 0 \left\{ C(x,0) = 0,\ 0 < x < L \right\}.$$

According to the adopted reasoning, these following hypotheses seem to be admitted by authors (1):

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*CCR 24 (2) 375-379 (1994).

**CCR 23 (3) 724-742 (1993).

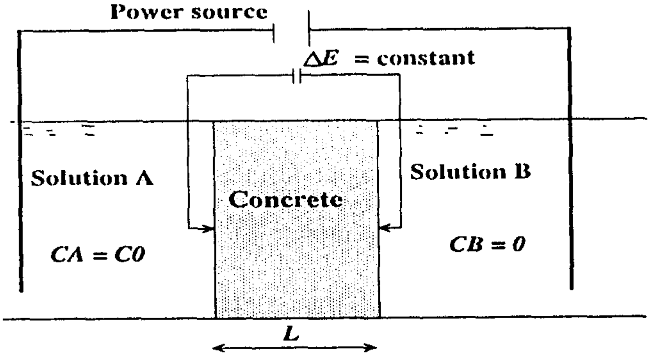

FIG. 1.
Ideal experimental arrangement according to imposed conditions of resolution.

- The sample of concrete is homogeneous;
- The convection and the interfacial phenomena that occur in concrete are neglected.

Considering the boundary conditions and the hypotheses defined previously, the diffusion process will be irreversible and one-dimensional. (Note that it is very important to plot chloride profile). The equation of the electro-migration (Fick's second law modified) is obtained by using the general theory of irreversible phenomena (3):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - KC \tag{1}$$

where:
D : diffusion coefficient, considered constant
K: parameter reflecting the reactions that occur in the concrete, taken into account in the simplest form. K is considered constant,

$V = \frac{Z_{Cl}F}{RT}\frac{|\Delta E|}{d}D$ (p 377), where d is the distance between the reference electrodes.

If $d > L$ (reference electrodes are placed in the solutions but not directly against the sample), our experiences show that there is a fall of potential in the media A and B. The sample does not undergo the difference of potential ΔE taken into account in calculation. Therefore, to maintain ΔE constant between the sides of the specimen, the use of a four electrodes arrangement (Figure 1) is indispensable. In this case d should be equal to L and

$$V = \frac{Z_{Cl}F}{RT}\frac{|\Delta E|}{L}D. \tag{2}$$

Analysis of Solutions Proposed by Xu and Chandra (1)

To illustrate solutions obtained by Xu and Chandra, concentration profiles of chlorides in non-dimensional terms are plotted on graph with numerical value given by the authors (p. 378), namely $\Delta E = 10$ Volts exerted across 1m, at 20°C, $D = 10^{-11}$ m²/s, $L = 0.1$ m and $K = 0.1V$

Note that K has not the same unit than V; it is just a numerical ratio between the two parameters. In transitory state, the solution proposed by authors is ((5), p 378):

$$\frac{C(x,t)}{C_0} = e^{\frac{V}{2D}x}\left[1-\frac{x}{L}-\frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\;\frac{Sin\frac{n\pi x}{L}}{\frac{V^2}{4D}+K+(\frac{n\pi}{L})^2D}\left(\frac{V^2}{4D}+K+(\frac{n\pi}{L})^2De^{-\left[\frac{V^2}{4D}+K+(\frac{n\pi}{L})^2D\right]t}\right)\right]$$

The concentration profiles are represented in Figure 2.

The expression corresponding to the steady state should be obtained from the previous relationship, by relating the time to infinity ($t \to \infty$). Hence Eq.6 p. 378 (1):

$$\frac{C(x)}{C_0} = e^{\frac{V}{2D}x}\left[1-\frac{x}{L}-\frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\;\frac{Sin\frac{n\pi x}{L}}{\frac{V^2}{4D}+K+(\frac{n\pi}{L})^2D}\left(\frac{V^2}{4D}+K\right)\right]$$

By taking $K = 0$, in Eq.6 (p. 378) (1), one has to obtain the stationary flow, expressed by the following equation:

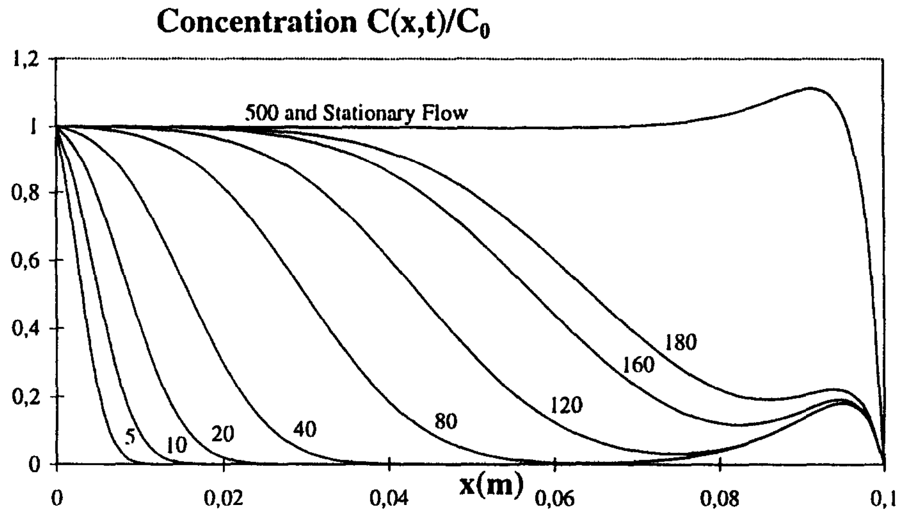

FIG. 2.

Distribution of $C(x,t)/C_0$ calculated by Eqs.5 and 6 (p.378) (1). The numbers in the graph express the time in days.

$$\frac{C(x)}{C_0} = e^{\frac{V}{2D}x}\left[1-\frac{x}{L}-\frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\,\frac{Sin\frac{n\pi x}{L}}{\frac{V^2}{4D}+(\frac{n\pi}{L})^2 D}\left(\frac{V^2}{4D}\right)\right]$$

This equation is different from the one proposed by the authors in the Figure 1, (p.377) for the stationary flow, which is incorrect.

For $K = 0.1\,V$, the concentration profiles corresponding respectively to steady and stationary flow are the same. To distinguish between them, it is sufficient to increase the value of K.

Figure 2 explains very clearly that the solutions (Eqs.5 and 6 p.378) of the authors are not correct given the boundary conditions and hypotheses of calculation. The diffusion phenomenon is irreversible given the fixed conditions, one can not have either:

- an increase of the concentration (increase of $C(x,t)/C_0$) through the sample. The ratio $C(x,t)/C_0$ has imperatively to decrease, or at least remain constant, when x increases,
- a ratio $C(x,t)/C_0 > 1$, whatever is x or t.

Mathematically, conditions of work impose, whatever the considered flow (transitory, steady or stationary):

$$\frac{C(x_1,t)}{C_0} \geq \frac{C(x_2,t)}{C_0} \quad \text{if } x_1 < x_2;\ x_1;x_2 \in [0,L] \text{ whatevert} > 0\,;$$
$$\frac{C(x,t)}{C_0} \leq 1 \quad \text{whatever } x \in [0,L].$$

These two conditions are not verified in solutions (Eq.5 and 6) of the authors (p. 378), as shows the previous numerical example.

Note that the solution (Eq.6) is valid at $x = L$. Authors show it clearly by calculating the flux at this point.

Let us now examine the solutions that we propose for the different states.

Resolution in Stationary and Steady State

The concentration of chloride will only depend on the variable of space. One notes that $C = \overline{C}(x)$, Eq.1 becomes:

$$D\frac{\partial^2\overline{C}}{\partial x^2} - V\frac{\partial\overline{C}}{\partial x} - K\overline{C} = 0 \tag{3}$$

Taking into account the boundary conditions, the solution of the Eq.3 is:

$$\frac{\overline{C}(x)}{C_0} = e^{\frac{V}{2D}x} \frac{\sinh(\frac{V}{2D}\sqrt{1+\alpha}\ (L-x))}{\sinh(\frac{V}{2D}\sqrt{1+\alpha}\ L)} \quad ; \quad \alpha = \frac{4KD}{V^2} \tag{4}$$

By considering that the chemical reactions are limited in time (which is likely), K tends to zero as the time increases. All chemical reactions will take place and the stationary flow is reached. The solution is thus written as follows:

$$\frac{\overline{C}(x)}{C_0} = \frac{1-e^{-\frac{V}{D}(L-x)}}{1-e^{-\frac{V}{D}L}} \tag{5}$$

Thus we find the solution proposed by the authors (Figure 1, p. 377).

Resolution in Transitory State

The equation (1) is solved in non-dimensional variables. Let us denote:

$x_+ = \frac{\pi x}{L}$; $\tau = \frac{L^2}{\pi^2 D}$; $t_+ = \frac{t}{\tau}$; $C_+ = \frac{C}{C_0}$; the Eq.1 becomes:

$$\frac{\partial C_+}{\partial t_+} = \frac{\partial C_+}{\partial x_+^2} - \frac{VL}{\pi D}\frac{\partial C_+}{\partial x_+} - \frac{L^2}{\pi^2}\frac{K}{D}C_+ \tag{6}$$

whose solution can be decomposed as follows:

$$C_+(x_+,t_+) = \overline{C}_+(x_+) + \tilde{C}_+(x_+,t_+) \tag{7}$$

Where:

$$\tilde{C}_+(x_+,t_+) = \sum_{n=1}^{\infty} F_n(x_+)G_n(t_+) \tag{8}$$

from Eq.6, 7, 8 we obtain the solution of equation of transfer:

$$\frac{C(x,t)}{C_0} = e^{\frac{V}{2D}x}\left[\frac{Sinh(\frac{V}{2D}\sqrt{1+\alpha}\ (L-x))}{Sinh(\frac{V}{2D}\sqrt{1+\alpha}\ L)} - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\frac{Sin\frac{n\pi x}{L}(\frac{n\pi}{L})^2 D e^{-\left[\frac{V^2}{4D}+K+(\frac{n\pi}{L})^2 D\right]t}}{\frac{V^2}{4D}+K+(\frac{n\pi}{L})^2 D}\right] \tag{9}$$

Discussion

(i) We notice that according to Eq.9, we only need to increase time ($t \longrightarrow \infty$) to find the steady state (Eq.4);

(Ii) From the steady state expressed by the Eq.4, we obtain the stationary flow (Eq. 5) by putting $K = 0$;

(Iii) The case of the pure diffusion ($\Delta E = 0$) is obtained for the different states by replacing $V = 0$ in the corresponding equations after approximating by Taylor expansion around zero, for the expressions in hyperbolic sinus. One can also put $V = 0$ in the Eq.1, then solve it according to the state considered: Eq.1 then becomes:

In transitory flow:

$$D\frac{\partial^2 C}{\partial x^2} - KC = \frac{\partial C}{\partial t} \tag{10}$$

that admits for solution:

$$\frac{C(x,t)}{C_0} = \left[\frac{Sinh(\sqrt{\frac{K}{D}}\,(L-x))}{Sinh(\sqrt{\frac{K}{D}}\,L)} - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\,\frac{Sin\frac{n\pi x}{L}\,(\frac{n\pi}{L})^2 D e^{-\left[K+(\frac{n\pi}{L})^2 D\right]t}}{K+(\frac{n\pi}{L})^2 D} \right] \tag{11}$$

In steady state:

$$D\frac{\partial^2 C}{\partial x^2} - KC = 0 \tag{12}$$

whose solution is:

$$\frac{C(x)}{C_0} = \left[\frac{Sinh(\sqrt{\frac{K}{D}}\,(L-x))}{Sinh(\sqrt{\frac{K}{D}}\,L)} \right] \tag{13}$$

In stationary flow (K = 0):

$$D\frac{\partial^2 C}{\partial x^2} = 0\ ; \quad \text{i.e}\ \frac{\partial^2 C}{\partial x^2} = 0 \tag{14}$$

that has for solution

$$\frac{C(x)}{C_0} = (1 - \frac{x}{L}). \tag{15}$$

For comparison, the numerical example of the authors is used to plot the concentration profiles for the different states computed with Eq.4 and 9 (Figure 3).

The plots of Figure 3 are analogous to those of Figure 2 (according to the authors). We notice that in the case of proposed solutions (Figure 3), there is no contradiction between hypotheses of calculation and concentration profile of chlorides. We also notice that from $t = 500$ days approximately, the profile is confused with that of the steady state (or stationary, if one neglects the chemical reactions).

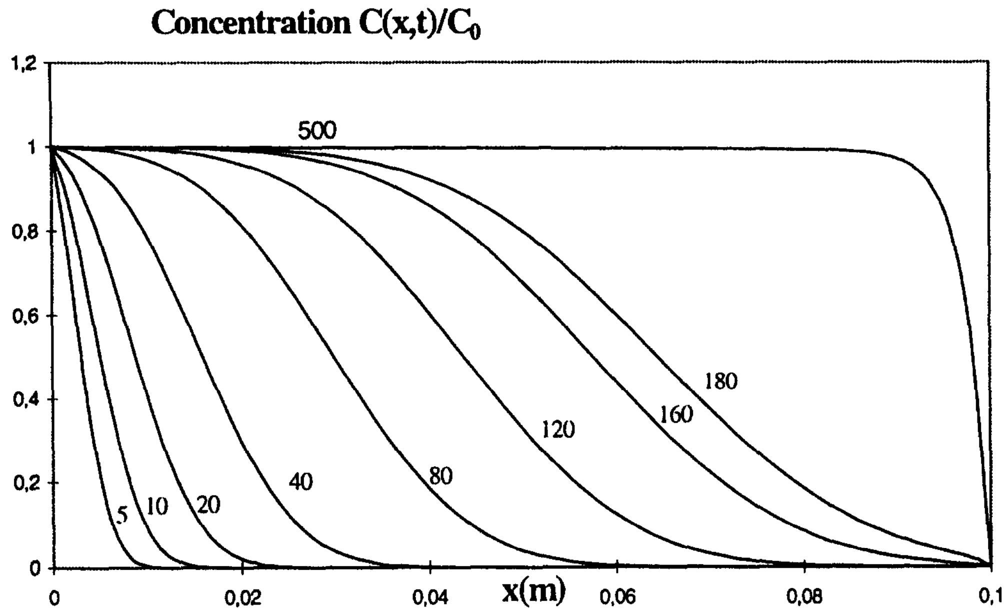

FIG. 3.
Distribution of $C(x,t)/C_0$ calculated respectively by Equations 4 and 9. The numbers in the graph express the time in days.

Conclusions

The aim of this paper is to complete the discussion of Xu and Chandra (1) on the article of Andrade (2). It remains to perfect the proposed study by an experimental validation. This requires a judicious protocol which is as close as possible to the conditions necessary to resolve the equation of transfer. The consideration of variations of parameters *D* and *K* will allow to refine proposed solutions. Furthermore, considering interfacial phenomena that occur in the concrete, known as "electrical double layer" would be welcome. Authors (Chatterji (4) and Zhang (5)) have shown that they have a considerable influence on the diffusion process.

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