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A Discussion of the Paper "CALCULATION OF CHLORIDE DIFFUSIVITY IN CONCRETE FROM MIGRATION EXPERIMENTS, IN NON-STEADY-STATE CONDITIONS" by C. Andrade, D. Cervigón, A. Recuero and O. Río

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The authors (1) dealt with a very interesting topic, but made some mistakes in their theoretical derivation and experimental arrangement.

1. Theoretical Mistakes

In their paper (1), the authors presented the following solution for the calculation of chloride diffusivity in concrete from the non-steady state process of electro-migration experiments:

$$C = C_S \operatorname{erfc} \frac{x}{2\sqrt{\frac{F\,Z\,\Delta E}{R\,T} D_{\text{app}}\, t}} \qquad [1]([17])†$$

where unless otherwise stated the same symbols as in (1) are used in this discussion. It is a pity, however, that the above solution is mathematically incorrect and physicochemically contradictory.

1) Mathematical incorrectness
   The authors deduced the similarity of the solutions between non-steady state diffusion and electro-migration from the similarity of the solutions between steady state diffusion and electro-migration. This deduction is, however, mathematically incorrect. According to the Nernst-Plank equation, the flux is

$$J = -D\frac{\partial C}{\partial x} - \frac{Z\,F}{R\,T} D\,C \frac{\partial E}{\partial x} \qquad [2]$$

   The analytical solution of Eq. [2] under a steady state condition is (2, 3):

$$J = D\frac{Z\,F\,\Delta E\left[C_1 \exp\left(\frac{Z\,F\,\Delta E}{R\,T}\right) - C_2\right]}{R\,T\,L\left[\exp\left(\frac{Z\,F\,\Delta E}{R\,T}\right) - 1\right]} \qquad [3]$$

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* CCR 24 (7), 1214 (1994).

† the number in brackets indicates the original equation number in (1).

If $|\Delta E|$ is large enough to make $\exp\left(\frac{Z F \Delta E}{R T}\right) >> 1$, that is, for electro-migration to dominate the process, Eq. [3] is reduced as

$$J = D \frac{Z F \Delta E C_1}{R T L} \qquad [4]$$

Whereas if $|\Delta E|$ is very small, $\exp\left(\frac{Z F \Delta E}{R T}\right) \approx 1 + \frac{Z F \Delta E}{R T}$, Eq. [3] becomes

$$J = D \frac{\left[C_1 \cdot \left(1 + \frac{Z F \Delta E}{R T}\right) - C_2\right]}{L} \approx D \frac{C_1 - C_2}{L} \qquad [5]$$

That is, the diffusion is dominant. It can be seen that Eq. [4] has an expression similar to Eq. [5], if $C_1 >> C_2$. This similarity, however, holds only under certain assumptions, i.e. a constant flux and a much lower concentration in the downstream cell. Therefore, it cannot be assumed to apply in other far different conditions, e.g. non-steady state conditions under which the flux J is not constant.

2) Physicochemical contradictoriness
It seems that the authors of the paper confuse the different terms in the Nernst-Plank equation. Under a non-steady state condition, the Nernst-Plank equation becomes

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} = D \frac{\partial^2 C}{\partial x^2} - \frac{Z F \Delta E}{R T L} D \frac{\partial C}{\partial x} \qquad [6]$$

if the electrical field is assumed constant. On the right side, the first term is contributed by diffusion and the second term by electro-migration. In their paper the authors stated at least twice that "assuming that the diffusion flow is negligible when compared with that generated by migration,..." but they gave the following formula which is completely contradictory to their assumption:

$$\frac{\partial C}{\partial t} = \frac{Z F \Delta E}{R T L} D_{\text{app}} \frac{\partial^2 C}{\partial x^2} \qquad [7]([15])$$

From the Nernst-Plank equation it can be seen that under the assumption of negligible diffusion Eq. [6] should become

$$\frac{\partial C}{\partial t} = -\frac{Z F \Delta E}{R T L} D \frac{\partial C}{\partial x} \qquad [8]$$

instead of Eq. [7], or Eq. [15] in (1).

The solution of Eq. [8] is very simple:

$$D = \frac{RTL}{ZF\Delta E} \cdot \frac{x_f}{t} \tag{9}$$

where x_f is the front of chloride migration after a test duration t. This is the reason why we previously suggested that the penetration depth should be measured to determine chloride diffusivity (4). It is a pity that the authors did not read our paper (4) very carefully and misconstrued our equation as "too empiric and cumbersome for practical purposes" (1). The term $1.061x_d^{0.589}$ in our paper (4) is a correction for the influence of diffusion in the electrical experiment, obtained from a numerical approach. In fact, our equation is just a simplification for practical purposes, although it is not an analytical solution. The analytical relationship between x_f and x_d involves solving an inverse error function and has recently been derived (5). With our method, all one needs to do is just to record the test duration t, measure the penetration depth x_d, and then calculate diffusion coefficient D by using even a portable calculator. Compared with the methods which require chloride profiles and a "curve fitting" technique, our method is much simpler and more practical. As Streicher and Alexander (6) commented, it appears "the most suitable of all the rapid chloride tests reviewed, on the basis of simplicity, duration of test, theoretical basis and versatility".

2. Experimental Mistakes

It is well known that in order to evaluate the parameters one should try to keep the experimental conditions similar to the boundary conditions in the theoretical analysis. In their experiments, however, the authors did not keep the chloride concentration in the catholyte constant (see Fig. 3 and Fig. 6 in the paper being discussed). It is obvious that their experiments did not meet the boundary conditions for both steady state and non-steady state electro-migrations. It is hard to believe that the authors can determine the "steady state" under a condition such that the concentrations on both sides of the specimen are continuously and appreciably changing, as shown in Fig. 6 in (1). The unstable flow and negative time lag found in Fig. 6 might be attributed to their incorrect experimental arrangement. In addition, the shapes of chloride distribution

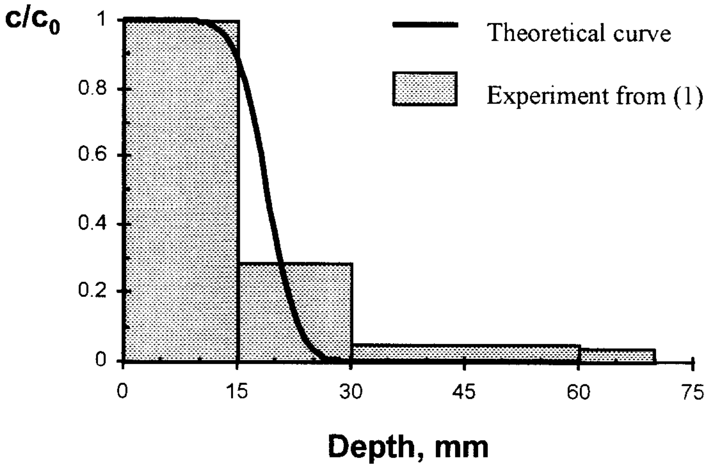

FIG. 1
Predicted profile of chloride distribution.

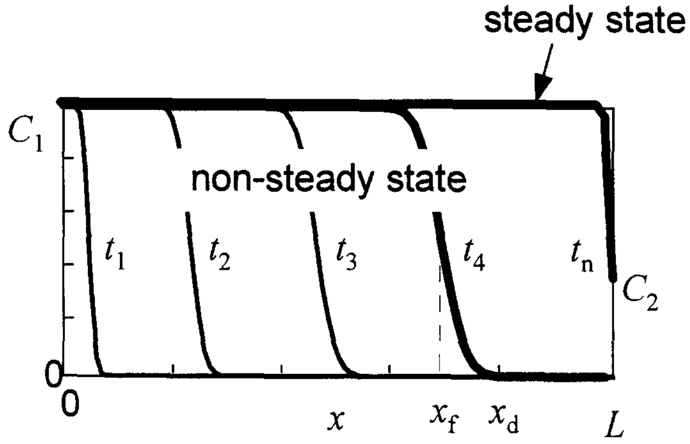

FIG. 2
Theoretical distributions of chloride ions after the electro-migration test.

reported in their paper seem uncertain due to a very rough sampling (15 mm of interval). From our experiment, the concrete with a w/c of 0.5 has a value of chloride diffusion coefficient about 15×10^{-12} m^2/s. This value can be used to predict the theoretical profile under their experimental conditions, that is, $\Delta E = 12$ V; $L = 0.135$ m; $t = 360000$ seconds (100 hours); and $T = 293$ K. The results are shown in FIG. 1. It is clear that the rough sampling in their study distorted the actual shape of chloride distribution.

Owing to these incomplete experiments, their results appear unconvincing.

3. Correct Description of Electro-migration

In fact, the analytical solutions to the Nernst-Plank equation for both steady state and non-steady state are available (3, 4). These solutions result in a chloride distribution as shown in FIG. 2. It can be seen that under a steady state condition, the chloride content is uniform almost throughout the specimen. This has been verified by Hauck's (7) experimental data, as shown in FIG. 3. Under

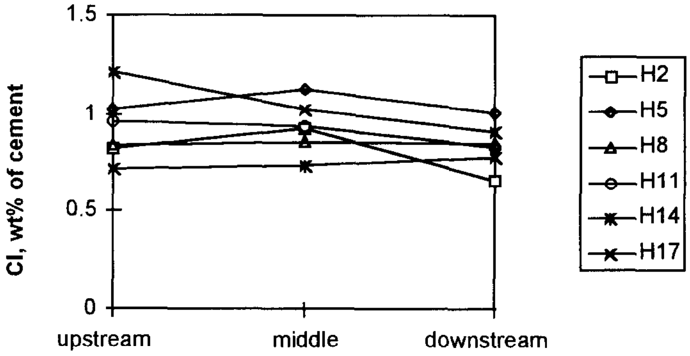

FIG. 3
Distributions of chloride ions after the steady state migration test, data from (7).

non-steady state conditions, the distributions vary with many factors, such as experimental conditions, properties of the specimen, and pore distributions. The latter will be discussed in the paper elsewhere (8).

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