



**A REPLY TO THE DISCUSSION OF THE DISCUSSION OF THE PAPER:  
 "CALCULATION OF CHLORIDE COEFFICIENT DIFFUSION IN CONCRETE  
 FROM IONIC MIGRATION MEASUREMENTS"\* BY O. AMIRI et al.**

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(Received April 15, 1997)

On behalf of Dr. Chandra, co-author of our paper\* under discussion, I would like to express our thanks to Drs. Amiri, Ait-Mokhtar and Seigneurin for their contribution to the understanding of the ion transport processes.

I appreciate the equation presented in the discussion, which may be correct though a strict prove is yet to give. But I cannot agree on the method of "prove" and the comment that the equation we presented was incorrect. First of all, I would like to point out that the analytical solution to a given mathematical problem may have various expressions depending on the approach used. Secondly, one should be cautious when trying to verify a closed solution by numerical calculations, noting that this type of calculation is **not** a prove. To make my point clear, I would like to brief some of derivations and features of the formulas.

**The Steady Flow State**

At this state,  $\partial C(x,t)/\partial t = 0$ . When adsorption or chemical reaction is absent, i.e.  $k = 0$

$$J = -D \frac{dC(x)}{dx} + VC(x) \quad (1)$$

where  $J$ , the flux, is a constant. Its homogeneous solution, i.e. when  $J = 0$  so that  $dC/dx = VC/D$ , is  $C(x) = A \cdot \exp(Vx/D)$ . Letting  $A$  be a variable of  $x$ , differentiating  $C(x)$  against  $x$  and rearranging for the case when  $J \neq 0$ , gives  $dA/dx = (-J/D) \cdot \exp(-Vx/D)$ . Hence  $A = A(0) + (J/V)(\exp(-Vx/D) - 1)$ , where  $A(0) = C(0) = C_0$ , the concentration at  $x = 0$ ; and

$$C(x) = \exp\left(\frac{Vx}{D}\right) \left( C_0 - \frac{J}{V} (1 - \exp\left(-\frac{Vx}{D}\right)) \right) \quad (2)$$

For simplicity, assuming  $C(l) = 0$ , one obtains

$$V = \frac{J}{C_0} (1 - \exp\left(-\frac{Vl}{D}\right)) \quad (3)$$

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

$V$  has a unit of  $\text{m} \cdot \text{s}^{-1}$ , and is the speed of the ions convection (under an electric field of 10 Volts per 0.1 m, and  $D = 10^{-11} \text{ m}^2/\text{s}$ , it is  $4 \times 10^8 \text{ m/s}$ ). Substituting Eq.3 into Eq.2 gives the equations in our paper (Eq3 and the equation in Figure 1 on p.377, paper<sup>\*</sup>), the latter is

$$\frac{C(x)}{C_0} = \frac{1 - \exp(-V(l-x)/D)}{1 - \exp(-Vl/D)} \quad (3a)$$

### About the Diffusion-Convection-Reaction Equation (Eq.5, paper<sup>\*</sup> p.378)

**Numerical Calculation** of this equation needs very high precision, for which I would like to mention only that its multiplication term  $\exp(Vx/2D)$  is a very large number. For example at an electric field of 10 Volts per 0.1 cm, it is nearly  $5 \times 10^8$  at  $x = 0.1 \text{ l}$ . Thus the calculation of the other parts, which will give very elegant differences, requires to use very large  $n$  (number of terms in the Fourier series) to obtain an accuracy no less than that to the 10th decimal levels (and higher) to make the result meaningful. And it is well known that Fourier series have non-continual points, i.e. for *Sinus* function, it is at the points where  $nx/l = \text{integer}$ , near which the values tend to be larger. I interpret the abnormal curve ends in Figure 2 of the discussion as due to erroneous calculation, as it is hard to explain the fact that curves in Figures 2 and 3 are identical at  $x/l < 0.7$ .

**To Prove an Analytical (or Closed) Solution to a Differential Equation**, it is required that a closed solution should satisfy: the differential equation, the initial condition and boundary condition for the specified problem. All the others, such as those mentioned under Figure 2 and the forms for special cases (Equations 10-15 in the discussion), are not necessary or not sufficient to prove the general validity of the solution. In this light, it is easy to see that our Eq.5 (paper<sup>\*</sup>) satisfies the boundary conditions,  $C(0,t) = C_0$  and  $C(l,t) = 0$ ; it also satisfies the initial condition,  $C(x,0) = 0$ , to prove this it may need the Fourier series

$$1 - \frac{x}{l} = \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi x}{l}\right) \quad (4)$$

With some careful calculations, it is also easy to find that the differential equation (Eq.1 of the discussion) is satisfied, and once again the expression Eq.4 is needed for the prove.

**There May be Different Forms for a Given Problem.** Our derivation can be briefed as follows:

- Let  $C(x,t) = v(x,t)\exp(\alpha x + \beta t)$ , where  $\alpha = V/(2D)$ , and  $\beta = -(k + V^2/(4D))$ . This choice of  $\alpha$  and  $\beta$  leads to  $\partial v(x,t)/\partial t = D \cdot \partial^2 v(x,t)/\partial x^2$ . It can be shown that  $v(x,t)$  satisfies the initial condition, but gives a non-homogeneous boundary condition at  $x = 0$ .
- Introducing a function  $p(t)\phi(x)$ , so that  $v(x,t) = w(x,t) + p(t)\phi(x)$ , to make  $v(x,t)$  have a homogeneous boundary condition. The simplest form is  $p(t)\phi(x) = \exp(-\beta t)C_0(1-x/l)$ . The problem has thus transferred to solving  $w(x,t)_t - Dw(x,t)_{xx} = F(x,t)$  (writing  $\partial w/\partial t$  as  $w_t$ ,  $\partial^2 w/\partial x^2$  as  $w_{xx}$ ), where  $F(x,t) = \beta \exp(-\beta t)C_0(1-x/l)$ . The solution to this equation is found by letting  $w(x,t)$  be the sum of two equations, i.e.

$w(x, t) = w^I(x, t) + w^{II}(x, t)$ , where  $w^I$  is a homogeneous equation with non-homogeneous initial condition, and  $w^{II}$  is a non-homogeneous equation with homogeneous initial condition:

$w^I(x, t)_t - Dw^I(x, t)_x = 0$ , at conditions:  $w^I(0, t) = w^I(l, t) = 0$ ; and  $w^I(x, 0) = -C_0(1-x/l)$ ;  
 $w^{II}(x, t)_t - Dw^{II}(x, t)_{xx} = F(x, t)$ , at conditions:  $w^{II}(0, t) = w^{II}(l, t) = 0$ ;  $w^{II}(x, 0) = 0$ .

The solutions to these function are obtained by conventional methods, and the results are:

$$w^I(x, t) = \sum_{n=1}^{\infty} \frac{-2C_0}{n\pi} \sin\left(\frac{n\pi}{l}\right) \exp\left(\frac{-n^2\pi^2 Dt}{l^2}\right)$$

$$w^{II}(x, t) = \sum_{n=1}^{\infty} \frac{-2C_0\beta}{n(D(n\pi/l)^2 - \beta)} \sin\left(\frac{n\pi}{l}\right) \left[ \exp(-\beta t) - \exp\left(\frac{-n^2\pi^2 Dt}{l^2}\right) \right]$$

And the final result was shown previously in our paper\*.

Please note that, the function  $p(t)\varphi(x)$  can be selected in other forms as well, e.g.  $\varphi(x)$  be a *Sinh* function (which may be a better choice, as we already know the steady-flow state distribution, Eq. 3a is proportional to the ratio of two *Sinh* functions). This is the fact why our solutions are in different forms compared to those by Amiri et al. And thus I cannot agree upon the comments made by Dr. Amiri et al. who judged the validity of our equations by what they look like. In fact, before we published our paper\*, numerical verifications were made to compare, e.g. the steady flow state expression with Eq. 3a shown above.

Regarding to comments on our selection of  $k/V = 0.1$  for calculation (by the semi-infinite space model), it should be stated that  $k$  is the reaction rate constant for the first order reaction (unit  $s^{-1}$ ) thus  $k/V$  has a unit  $m^{-1}$ . This value of  $k$  for the example mentioned ( $4 \times 10^{-9} s^{-1}$ ) was in fact too small, and could have been selected more reasonably according to the real reaction rate. But more exploring into the reaction rate is beyond my scope here.

### Remarks

In practice, for the problem of diffusion of ions under an electric field, with or without chemical reaction, it is much easier to use the closed solution for the semi-infinite space (Eqs. 7 and 8 in paper\*. I would like to take this chance to note that the "solutions" proposed in the reply to our discussion by Prof. Andrade are mathematically wrong.). It is valid as long as there is no ion migrates out of the specimen.

On the other hand, the solution for the steady flow state, Eq. 3a shown here, is preferred for the cases where the steady flow state is reached quickly, e.g. specimen is thin or poor in quality (diffusion coefficient is high), or is subjected to a high electric potential (note please: this will increase the temperature thus reduce the viscosity of pore solution and increase the diffusion rate, which makes analysis more difficult, is not a good alternative).

The analytical solutions to the problem in a finite space, such as that we previously showed and that presented by Dr. Amiri et al. in the discussion, or those yet to be derived for more complicated boundary conditions, may find their use in some cases to verify the numerical calculations (not the other way around), and to estimate the reaction rate. However, the calculation error must be carefully watched out and taken care of.