Pergamon

Cement and Concrete Research, Vol. 25, No. 5. pp. 1138-1144, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in the USA. All rights reserved
0008-8846/95 $9.50+.00

A Reply to the Discussion by L. Tang and L.-O. Nilsson of the Paper "CALCULATION OF CHLORIDE DIFFUSIVITY IN CONCRETE FROM MIGRATION EXPERIMENTS IN NON-STEADY STATE CONDITIONS"

C. Andrade, C. Cervigón, A. Recuero and O. Río
Institute of Construction Sciences "Eduardo Torroja"
Serrano Galvache, s/n 28033 Madrid, Aptdo. 19002
28020 Madrid, Spain

The authors would like first to thank the interest taken by Tang and Nilsson on their paper. This would enable us to extend the arguments and clarify better our contribution. We will reply all points of the discussion on the same order.

1. Theoretical mistakes

Regarding theoretical mistakes, we have to start saying that "electro-migration" is a term not used in electrochemistry, Migration means by itself alone "ionic movement due to the action of an electrical field". Although the term migration is sometimes used with the equal meaning of diffusion, this is theoretically incorrect. For electrochemists, "diffusion" is the motion due to a concentration gradient as driving force, and "migration or electro-diffusion" is the motion due to an electrical field as driven force.

1) Mathematical incorrectness

In the first part of this paragraph T&N conclude exactly the same than us, in (1) but using a mathematical way to reach a similar conclusion. That is, T&N state that if $\Delta E >> 1$, the migration term on Nernst-Plank equation dominates, and therefore the diffusion (and we add, the convection) ones may be neglected, whereas if ΔE is very small then, the migration term becomes negligible. This is indeed an oftenly used approximation in electrochemistry (2,3), and that is why we have mentioned it in our paper referring to the first paper of C. Andrade (4) on the subject, in which it was considered this argument as a basic simplifying assumption. We cannot kindly understand then why T&N say that we have an error when they now agree with us.

Perhaps it is because they end the paragraph stating that this argument cannot be applied to non-steady-state conditions. This is consistent with their paper (5), already discussed in ours (1). However, they do not justify why the same argument cannot be applied to the non-steady-state conditions. In fact, it is currently applied when solving electrochemical processes (2,3).

CCR 24(7) 1214-1228 (1994)

Let us continue, because in next point we will justify our assumptions that we think were not understood by T&N.

2) Physicochemical contradictoriness

First T&N express their doubts of our ability of understanding the meaning of Nernst-Plank equation. We kindly remind them our first presentation applying an electrochemical background to the "Rapid chloride Permeability Test" during our meeting of the RILEM TC-116: "Permeability of concrete" of which Prof. Nilsson is also a member. There C. Andrade presented some fundamentals on Nernst-Plank equation and produced two internal papers in May 1990 (6) and August 1992 (4). Afterwards she presented her fundings in (7) and she produced the first publication in March 1993 (8) where the electrochemical principles of migration were commented. Nobody before have called Nernst-Plank equation by the name of its authors. We have been also the first introducing terms such us "catholyte" or "anolyte", or even our insistence of using "migration", such as. It seems difficult that we do not understand the meaning of Nernst-Plank equation, when we have been the first to relate it to the specific problem of chloride permeability in concrete.

This does not mean actually that we cannot be erroneous, but it illustrates (together with our experience in the corrosion field) that our physicochemical background is sound enough to deduce that our errors might be mathematical, but not of electrochemical nature.

Concerning the solution that T&N present in their equation \6\ it is not the correct one as being incomplete. The complete Nernst-Plank equation in non-steady-state conditions (assuming D= constant) is:

$$-\frac{\partial J}{\partial x} = -\frac{\partial C}{\partial x} = D\frac{\partial^2 C}{\partial x^2} + \frac{ZF}{RT}D\,[\frac{\partial C}{\partial x}\,\frac{\partial E}{\partial x} + C\frac{\partial^2 E}{\partial x^2}] \qquad [1]$$

It may be deduced that, the solution of this equation is not easy, and in fact very difficult without knowing the dependence of ∂E/∂x with x (the dependence of electrical field with x). This difficulty has been traditionally recognized (9). In our understanding a rigourous solution of equation [1] has not been still achieved. The main difficulty comes from the need to know the ion concentrations at every point, and the need to complete the set of equations with:

$$\frac{\partial^2 E}{\partial x^2} = -\frac{4\pi}{\epsilon}\,\Sigma\, n_i z_i \qquad [2]$$

where ϵ= dielectric constant of the electrolyte.

In consequence the only way to solve expression [1] is to try simplifying assumptions.

Let us analyze those considered by T&N. On one hand they have forgotten the term ($\partial^2 E/\partial x^2$ and on the other hand, they have considered $\partial E/\partial x = \Delta E/L$ and $\partial x/\partial t = x_f/t$.

This last leading to \9\ is really too crude and empiric as we said (1), even for practical purposes as they try to justify. In addition equation \9\ of T&N does not enables the chloride profile to be deduced. They mention that this is an advantage as avoids the need of curve fitting, but for the same reason, several chloride profiles could fit into their solution, which might give different chloride concentrations at the rebar surface.

As well it has to be mentioned that the use of the term ΔE/L contradicts the assumption of semi-infinite media. This is also a limitation that may be applied to Xu and Chandra (10) solution. These last authors had to assume it due to the difficulties of a rigourous solution of equation [1].

In summary, T&N propose equation \8\ and say that the solution is going to be given in a near future. We wait for the solution, as equation \9\ does not seem to us enough suitable or accurate.

In fact, a rigourous solution of Nernst-Plank equation in non-steady-state conditions implies the knowledge of how the electrical field varies with the distance, due the variation of chloride concentration. We decided therefore, to solve the problem not by solving accurately Nernst-Plank equation, but rather by using the concept of ionic mobility. The solution we propose is first conceptual and then, mathematical.

In our preliminary work we arrived to the same point of equation \8\ of T&N but we did not like to follow solving it as they do. We decided to go back trying to achieve an analytical equation whose numerical one was known enough. That is, to try to find an analytical formula already solved.

The way we propose to solve the problem, and it represents the most original part of our paper, is based in the pysico-chemical concept of "ionic mobility", $\mathbf{u}_i$ which is well known (2, 3) to be:
being the terms those described in previous papers (7)(11), and D_i= Ddif= Diffusion Coefficient of species i. It represents the limiting velocity of an ion submitted to an electrical field of a strength unity (1V/cm). It also may be described as the acceleration suffered by a diffusing ion when an external electrical field is applied to the solution.

$$u_i = \frac{zFD_i}{RT} \qquad [3]$$

Therefore, if expression [3] is multiplied by the external field ΔE, it results the expression:

$$D_{mig} = u_i \Delta E = \frac{zFD_{dif}}{RT} \Delta E \qquad [4]$$

being Dmig (named Dapp in our equations [16] and [17] (1)) the result of multiplying the Diffusion Coefficient, D_i, by the accelerating term ZFΔE/RT derived from the concept of ionic mobility.

This expression [4] if divided by the distance l gives the ionic velocity, and multiplied by the concentration, gives the flow J_i. That is:

$$J = u_i . C_i . \Delta E / l \qquad [5]$$

In summary, a random walk of an ion moving due to a concentration gradient, may be accelerated and driven by the application of an electrical field. This field has an accelerated action that is expressed by the concept of "mobility".

Therefore, if we have a test with the geometrical arrangement of the ponding one, we may accept that the law regulating the motion is the same than that of the diffusion but with a multiplying accelerating term. Thus, it results our expresion:

$$\frac{\partial C}{\partial t} = \frac{ZF}{RT} D_{dif} \Delta E \frac{\partial C^2}{\partial X^2} \qquad [6]$$

whose solution is well known for the a semi-infinite medium with the usual boundary and initial conditions (3).

Furthemore, this expression is dimensionally and fundamentally the same that equation \8\ of T&N (that we have already mentioned we also obtained in our previous work). Let us explain the similarities and why we prefered [6].

A careful comparison of both allows inmediately to observe as aforementioned, that dimensionally they are identical. That is, both may be correct. The only difference appears in that $1/L\ \partial C/\partial x$ is substituted in ours by $\partial^2 C/\partial x^2$. This is mathematically feasible, and in addition it has the advantages of: a) considering in some way the variation of ΔE along the distance ($1/\partial x$ instead of $1/L$), that is, the electrical field is not taken as homogeneous, and b) it does not contradict the assumption of semi-infinite medium by introducing **L** into the solution.

The other two main advantages in favour of our solution that decided us to propose equation [6] instead of \8\ are:

1) It has a very well known solution, familiar for concrete specialists.
2) The principle can be applied to any other type of test whose diffusion expressions were already solved or known. This is in fact the main advantage. A paper will appear soon in this Journal (12) with the calculation of chloride removal solved by the application of the mobility concept.

2. Experimental mistakes

Few words on this last discussion point as it has been extensively addressed in (13) to which we refer the interested readers. We know indeed the conditions to better reproduce initial and boundary conditions and we criticize our own and other (including T&N experiments, that also have some deviations from the theoretical optimum conditions) accuracy. These limitations have to be taken into account but, our interest now is focussed to fit into an error as small as possible when compared with parallel experiments of pure diffusion.

Assumed this, in this paragrah T&N consider a D value of 15×10^{-12} m^2/s (without describing from which kind of experiment they deduce this value) and they apply it to our experiment (1). In our experiments of natural diffusion we obtained a value of 8.1×10^{-12} m^2/s for concrete C1 and of 5.1×10^{-12} m^2/s for concrete C2. In the parallel migrations experiments we obtained respectively 2.37/3.63 for C1 and $1.38/2.90 \times 10^{-12}$ m^2/s for C2. We think that our approximation is good enough. We cannot consider 15×10^{-12} m^2/s a better one.

At this respect, what we would like to stress is the fact that we always compare our results with parallel experiments of natural diffusion (13)(14), comparison that until now has not been offered by T&N. The results are not "convincing" or "not convincing", but rather they fit or not in a reference test. Only such a comparison will validate any solution proposed.

Correct description of "Electro-migration"

Here T&N insist in their solution (4), on what we hope to have presented more arguments of its empiric character (they recognize this in present discussion) or approximate nature. About the solution given in (10) by Xu and Chandra, we already mentioned: a) its cumbersome character, b) it is also an approximation and c) due to the need of simplifying, it has the also contradiction to introduce the term L when assuming a semi-infinite media.

In addition, looking at X&C figure (10) their equation seems to predict a too slow process if we compare with experimental results. Thus, they have $C_x/C_s = 0.2$ at only 7 cm after 180 days of application of the voltage difference in a concrete of $D = 10^{-12}$ m^2/s. In our experiments such a reduction is obtained for a concrete of similar D in about 10-15 days. Perhaps this is due to they consider the simultaneous diffusion in opposition to migration flow, or because the equation definitively does not reproduce the real behaviour.

CONCLUSIONS

In present discussion T&N accept now the feasability of neglecting the diffusion term as a simplification in the case of steady-state conditions. They do not accept for non-steady state, although they use the neglection to arrive to their equation \8\ which results:

$$\frac{\partial C}{\partial t} = \frac{ZF}{RT} D \frac{\Delta E}{L} \frac{\partial C}{\partial x} \qquad \backslash 8 \backslash$$

We do not take into consideration their step going into their equation \9\ as being mathematically too crude.

This equation results dimensionally and fundamentally similar to that we presented:

$$\frac{\partial C}{\partial t} = \frac{ZF}{RT} D \Delta E \frac{\partial^2 C}{\partial x^2} \qquad [6]$$

Our equation supposes a new and original way of solving a non-steady-state condition. It is deduced not as a solution of Nernst-Plank equation, but as the appplication of the concept of "ionic mobility" to the particular case. The rigourous solution of Nernst-Plank equation is still too far of our possibilities.

Being new the approach, it is risky, however the experimentation carried out until now confirm its suitability to fit into experimental results (13)(14) as compared with parallel natural diffusion tests.

The main advantages that our equation [6] presents are:

1) The concept of ionic mobility can be applied to any other type of test with well defined initial and boundary conditions already solved as a diffusion problem.

2) It considers a kind of non homogeneous electrical field along the distance (by considering the term $1/\partial x$ instead of $1/L$). This means that considers a non homogeneous conductivity, that is, it takes into account the progressive penetration of chlorides.

3) The numerical solution of equation [6] is already known and familiar for concrete specialists.

Finally the authors would like to say that they observe with pleasure that an increasing number of concrete researchers refer now to Nernst-Plank equation as if they have used it forever. However, its interpretation and mathematical solution are not as easy as it may be deduced from its apparent simplicity. It seems better to try to fit into a sound conceptual background than to try a mathematical solution whose electrochemical meaning may be incorrect. At this respect much more work is needed in the future, as the solutions used up to now in the literature applicable to semi-infinite media, may not be suitable for the particular geometrical conditions of concrete specimens (ponding test).

ACKNOWLEDGEMENTS

The first author would like to thank J.M. Diez, for the comments given to present paper.

BIBLIOGRAPHY

(1) C. ANDRADE, M.A. SANJUAN, A. RECUERO, O.RIO - Cement and Concrete Research, vol. 24, no. 6, pp 1214-1228 (1994).

(2) A.J. BARD, L.R. FAULKNER - Electrochemical Methods. Fundamentals and Applications - Jon Wiley & Sons Ed., (1980).

(3) J.O'M. BOCKRIS, A.K.N. REDDY - Modern Electrochemistry - Plenum Press Ed. New York (1974).

(4) C. ANDRADE - Calculation of chloride diffusion coefficients in concrete from ionic measurements - Internal Paper of Rilem TC-116 "Permeability of concrete" - Ag. 1992.

(5) L. TANG, L.O. NILSSON - ACI Materials Journal 89, no. 1 pp 49-53 (1992).

(6) C. ANDRADE - Brief comments on electrical methods used in concrete for measuring permeability - Internal Paper of Rilem TC-116: "Permeability of concrete" May 1990.

(7) C. ANDRADE - Int. Conference on "Structural Improvement through corrosion Protection of Reinforced concrete", London U.K. Institute of Corrosion, June (1992).

(8) C. ANDRADE - Corrosion-93, Nace, paper no. 319 - New Orleans, USA (1993).

(9) F. CONTI, G. EISENMAN - Biophys. J. vol.5, pp 247-256 (1965).

(10) A. XU and S. CHANDRA - Cement and Concrete Res. vol. 24, no. 2, pp.375-379 (1994).

(11) C. ANDRADE - Cement & Concrete Research, vol. 23, no. 3 (1993) 724-742.

(12) C. ANDRADE - Cement & Concrete Research & Concrete Research (in press).

(13) C. ANDRADE , M.A. SANJUAN - Advances in Cement Research vol. 6, no. 23, July pp127-134 (1994).

(14) C. ANDRADE, C. ALONSO, M. ACHA - Int. Conference on corrosion and Corrosion Protection of steel in concrete. Sheffield (U.K.) July, pp.783-793, 1994.