Pergamon

Cement and Concrete Research, Vol. 28, No. 5, pp. 773–775, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00021-0

DISCUSSION

A DISCUSSION OF THE PAPER "PRESENCE AND POSSIBLE IMPLICATIONS OF A MEMBRANE POTENTIAL IN CONCRETE EXPOSED TO CHLORIDE SOLUTION" BY J.-Z. ZHANG AND N.R. BUENFELD[1]

S. Chatterji
Carl Bernhardsvej 13B; St. 4 DK-1817 Frederiksberg C, Denmark

(Received October 17, 1997)

Drs. Zhang and Buenfeld are to be congratulated for their measurement of membrane potential across mortar specimens. However, in their discussions they have not done full justice to the results. As I understand, the results give much more information. In the following I would like to draw attention to some of them. The results using KCl solutions will be discussed, although similar points could be made using those of NaCl solutions.

For an easy reference I have first enumerated some salient points of the experimental technique used and of the results obtained.

1. In the experimental setup a 10-mm thick mortar specimen separated 0.1 M KCl and 1 M KCl solutions. Both KCl solutions were renewed on the 10th day. Two calomel electrodes were used to measure the potential difference across the specimen.
2. The potential measurements showed that in the first lot of solutions the initial potential was -45 mV. The potential then dropped steeply to about -25 mV by the 4th day and then slowly to about -22 mV by the 10th day when the solutions were renewed. In the renewed solutions the initial potential was about -35 mV, which dropped to -27 mV by the 12th day, then to about -25 mV by the 16th day.

The use of KCl solutions has substantially eliminated the liquid junction potentials between KCl solutions and the pore solution in the sample. In the experimental setup two calomel electrodes jointly acted as (Cl_2/Cl^-) electrodes (1). That means the whole setup is equivalent to a concentration cell with transference (2). The E.M.F., E, of such a cell is given by Eq. 1 where:

$$E = -\,t_+ \frac{(\nu_+ + \nu_-)}{\nu_-} \frac{RT}{z_- F} \ln \frac{a_2}{a_1} \tag{1}$$

t_+ is the transference number of K^+ ion, ν_+, ν_- are the number of positive and negative ions produced by 1 mol of KCl, z_- is the valency of chloride ion, R and T are gas constant

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[1] Cem. Concr. Res. 27, 853–860 (1997).

and the temperature respectively, F the Faraday constant, and $a_i s$ are activity of the KCl solutions; a_1 being the more concentrated solution. The activity of KCl solutions is given in (3). In pure KCl solutions, t_+ is 0.5. At 25°C the calculated E is -53 mV. The calculated value compares favourably with the first measured potential of -45 mV, and supports the idea that the setup acted as a concentration cell with transference.

The fall of the measured potential with time may be due to either 1) a decrease in the activity ratio or 2) a decrease in t_+. However, a decrease in the activity ratio within 4 days could be ruled out as that will mean a high rate of diffusion of chloride ion through the mortar specimen. That leaves only t_+. A decrease in t_+ means that K^+ is no longer carrying its share of electric charges, i.e., some other ion(s) is taking part. The results show that by the 10th day the contribution of K^+ to t_+ has dropped to about 0.25.

A review of the literature shows a number of reports claims that the steady state diffusivity of all alkali ions, including K^+, through cement-based materials is about half that of chloride ions (4). A recent review has shown that in a natural diffusion, like that used by Zhang and Buenfeld, Ca^{2+} co-diffuses with K^+ and Cl^- to the downstream side and OH^- ion to the upstream side (5). The decrease in the diffusivity of K^+ and co-diffusion of Ca^{2+} explains the drop in the transference number of K^+ to about 0.25 and consequent drop in the measured potential.

The difference between the starting potentials of the first set of solutions and the potentials after the renewal could be due to the altered state of pore solution caused by the first stage of diffusion. Note also that the both sets of potentials approach the same ultimate potential of about -20 mV as is expected in the steady state.

The following inferences may be drawn:

1. In the case of natural diffusion, the Nernst-Plank equation could not be set up for a single ion. In this case a set of simultaneous equations for all the ions involved has to be set up and solved. In setting up the equations the direction of movement of each ion, e.g., the upstream movement of OH^- ions, has to be taken into account. This involves mathematical difficulties.
2. The variations in the transference numbers of different ions with the variation in the composition of electrolyte solution in the membrane have to be taken into account. In the original formulation of the Nernst-Plank equation for very thin membrane, the transference numbers of different ions were taken to be constant. In solution electrochemistry this assumption could be satisfied by keeping the electrolyte composition constant by stirring, which could not be done in a thick membrane.
3. The near-identity of the measured initial and calculated membrane potentials indicates that at the initial stages of diffusion the membrane potential is not affected by the electrical nature, e.g., charged or uncharged, of the membrane. Measurement of membrane potential at later stages of diffusion gives information on the electrical nature of a membrane.
4. Equation 1 shows that if the concentration of the downstream solution is kept nearly constant, as is the practice in the diffusion cell experiments, the membrane potential E will vary with the variation in the concentration of the upstream side solution. This variation will in its turn alter chloride ion transport through the specimen, i.e., the $D_{ef.}$ is concentration-dependent as has earlier been shown (6).

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