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DISCUSSION

A REPLY TO THE DISCUSSION BY S. CHATTERJI OF THE PAPER "PRESENCE AND POSSIBLE IMPLICATION OF A MEMBRANE POTENTIAL IN CONCRETE EXPOSED TO CHLORIDE SOLUTION"[1]

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The authors acknowledge the contributions of Dr. Chatterji in the field of ion transport in cementitious materials (1) and thank him for his interesting discussion of our paper. In his discussion, Chatterji re-interprets the origin of the membrane potential and considers the effects of possible ion transport processes on the potential. We agree with Chatterji that the results reported may contain more information than we discussed, especially in relation to diffusion cell testing and the ion transport mechanisms involved. However, we feel that the theory of concentration cell with transference proposed by Chatterji in the discussion is not appropriate and we must therefore question the validity of the inferences drawn in the discussion.

Chatterji suggests that the experimental setup is equivalent to a concentration cell with transference in which the reference electrodes used to measure the potential are reversible to Cl^- ions in the solutions (2). Therefore the measured membrane potential would be the electromotive force of a concentration cell resulting from the concentration difference of the two KCl solutions. We disagree with this.

To clarify the problem, it is necessary to further explain the experimental setup. There are several types of potential possibly arising in an electrochemical cell setup, in particular, junction potential between a reference electrode and a solution, membrane potential, and concentration cell potential. To measure the membrane potential of the mortar specimen, the electrochemical cell and reference electrodes were carefully designed and selected to exclude or minimize other possible potentials. First, KCl was used because K^+ and Cl^- ions have similar self-diffusion coefficients in water. If a membrane has no permselectivity to Cl^- or K^+, there would be no membrane potential across the membrane. Furthermore, in a normal OPC pore solution, the concentration of K^+ is far higher than that of Na^+; the use of KCl reduces the changes in pore solution composition and consequential effects due to diffusion of cations. Second, two identical calomel electrodes (commercially available) that employ saturated KCl solution were used. The concentration of the KCl used in the reference electrodes is not important as long as the two electrodes have the same KCl concentration. The reasons for choosing calomel electrodes were: 1) that the electrode has negligible liquid junction potential, and 2) that the electrolyte (KCl) inside the electrodes is the same as that in the test cell so that the possible liquid junction potential

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

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caused by different electrolytes interfacing was avoided. The potential between the two calomel electrodes was monitored via a potentiostat and the potentials of the two electrodes were regularly checked against another calomel electrode during the test period. Therefore the experimental setup was typical of one for measuring membrane potential (3).

As described by Chatterji, in a concentration cell measurement, the reference electrode surface is directly in contact with the cell solution and the electrode reaction should be reversible to one of the ions in the cell. In addition, the potential of a concentration cell (described by Eq. 1 in Chatterji's discussion) depends on not only the activity ratio, but also on which ion the electrode reaction is reversible to. Therefore we feel that, in Chatterji's discussion, the experimental setup for measuring membrane potential was mistakenly treated as one for measuring concentration cell potential. As a result, the interpretation of the results and the inferences drawn based on the concept of a concentration cell are not valid.

The cause of the membrane potential observed has been explained in the paper. It is mainly due to the difference in mobility of ions (e.g. Cl^- and K^+) in the mortar specimen. To maintain macroscopic neutrality of the cell, an electric field is established across the membrane and then a steady state of KCl transport is finally reached in which K^+ and Cl^- carry the same amount of charge across the mortar specimen from the higher to the lower concentration side (for simplicity, transport of other pore solution ions is not taken into account). This is actually equivalent to an internal liquid junction potential that is described by Eq. 1 in the paper for a simple binary monovalent electrolyte (e.g., KCl):

$$\Delta\varphi = \frac{RT}{F}\left(\frac{D_s^+ - D_s^-}{D_s^+ + D_s^-}\right)\ln\frac{C_2}{C_1} \tag{1}$$

It can be also expressed as:

$$\Delta\varphi = \frac{RT}{F}(\tau^+ - \tau^-)\ln\frac{C_2}{C_1} \tag{2}$$

where τ^+ and τ^{2-} are the transference numbers of cation and anion. This indicates that the membrane potential is caused by the difference in transference numbers of the Cl^- and K^+ ions. As K^+ and Cl^- have similar mobility (or self-diffusion coefficient or transference number) in water, the different transference numbers in the mortar specimen should be attributed to the electrically charged nature of cement paste pore surfaces. Regarding the variation of the measured membrane potential, it is felt that more experimental work is needed to allow an acceptable quantitative interpretation, taking account of other processes involved, such as chloride binding and pore solution leaching.

There are many situations where the membrane properties of cementitious materials are believed to influence ion transport processes and, where possible, membrane potentials should be measured when studying these processes. The influence of membrane potentials on chloride diffusion into concrete is now being investigated by the authors under UK EPSRC Grant L40304.

References

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