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PRESENCE AND POSSIBLE IMPLICATIONS OF A MEMBRANE POTENTIAL IN CONCRETE EXPOSED TO CHLORIDE SOLUTION

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ABSTRACT

Membrane potentials of between 20 and 45mV have been measured across OPC mortar specimens housed in chloride diffusion cells. Although previous research has indicated the membrane nature of hardened cement paste, this is believed to be the first time that membrane potentials for cementitious materials have been measured and reported. Electric fields of this magnitude have a strong influence on chloride ion transport, suggesting that they may need to be taken into account in the interpretation of chloride diffusion test results and in the prediction of chloride profiles. © *1997 Elsevier Science Ltd*

Introduction

Membranes. By definition, membranes have a porous structure with continuous pores in which ion transport takes place and the pore surfaces are charged by fixed ion groups with a particular polarity. As a result, membranes show physicochemical phenomena in relation to ion transport, which do not exist in non-membrane materials, such as membrane potential, permselectivity and electro-osmosis.

Membranes show selective permeability to ions of specific sign. For example, in a negatively charged membrane, reduced mobility of cations is observed. To maintain macroscopic electrical neutrality, an electric field is established across the membrane and this accelerates the cations and decelerates the anions. For a binary monovalent electrolyte, such as sodium chloride solution, once steady state conditions are reached, the diffusion coefficients of the cation and anion are equal (defined as D_s in this work) and the potential established can be expressed as (1):

$$\Delta \varphi = \frac{RT}{F}\left(\frac{D_s^+ - D_s^-}{D_s^+ + D_s^-}\right) \ln \frac{c_2}{c_1} \tag{1}$$

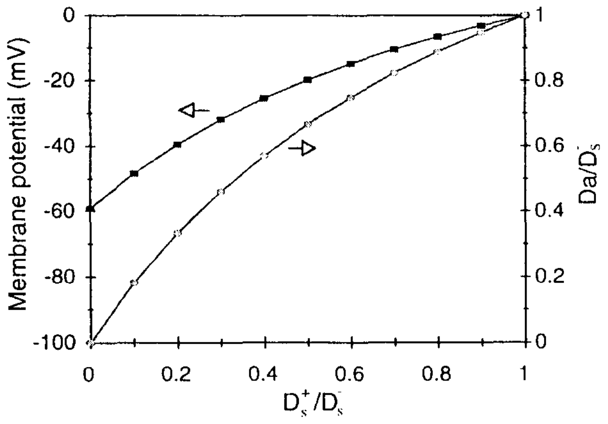

FIG. 1.
Dependence of membrane potential and D_a on self diffusion coefficients.

where $\Delta\varphi$ is the membrane potential, R the gas constant, T the absolute temperature, F the Faraday constant, c_1 and c_2 the activities of the solutions separated by the membrane and D_s^+ and D_s^- the self diffusion coefficients of the cation and anion in the membrane respectively; (self diffusion coefficients characterise ion diffusion in the absence of a membrane potential). In Fig. 1 the membrane potential is shown as a function of D_s^+ / D_s^- for a 10:1 activity ratio in the diffusion cell test.

The diffusion of ions within a membrane as the result of an electric field, is described by the Nernst-Plank equation as:

$$j_i = - D_i \left(\frac{\partial c_i}{\partial x} + \frac{FZ_i}{RT} c_i \frac{\partial \varphi}{\partial x}\right) \qquad (2)$$

where j_i is the flux of ion i. It is clear that ion transport in a membrane is controlled by both a concentration gradient and an electric field.

An important feature of ion transport in an electrolyte is that the transport of a particular sign of ions is affected by the presence of other ions. This becomes pronounced in membrane materials. When a steady state is reached in a diffusion cell test, the measured D_a may be expressed as:

$$D_a = D_s^- D_s^+ \frac{Z^- + Z^+}{Z^- D_s^- + Z^+ D_s^+} \qquad (3)$$

where Z^- and Z^+ are the valencies of cation and anion. The dependence of D_a on D_s^+ and D_s^- is also shown in Fig. 1.

Evidence of Membrane Properties of Cementitious Materials. Hydrated cement paste has a fine pore structure with pore sizes ranging from nanometres to microns. Ion transport takes place through this pore structure and is inevitably influenced by the physical and chemical states of the pore surface. The presence of a surface charge on the surface of hydrated cement has been confirmed directly by zeta potential measurement (2-4) electrokinetics (4,5) and chemical adsorption tests (6). The value and the sign of the surface charge has been found to depend on binder type (3,6,9) and electrolyte concentration (8), pH and composition (9,10). The membrane-related phenomenon of osmotic pressure has also been observed in cementitious materials (11). Hydrated cement paste certainly interacts with both anions (12) and cations (13,14) to reduce their rate of diffusion. Several studies have produced diffusion cell results that suggest that cations are more affected than anions (13-15), indicative of membrane behaviour. The authors are not aware of the membrane potential of a cementitious material having been measured and reported previously, nor of any work into the wider implications of membrane effects in concrete.

Experiment

A 100mm diameter, 50mm thick OPC mortar cylinder was cast with free water/cement ratio of 0.45, sand/cement ratio of 2.5 and maximum aggregate size of 2.36mm. It was cured in a sealed condition until an age of 28 days, stored at 86% relative humidity for 2.5 years. 10mm thick (100mm diameter) disks were then cut from its centre and these were then distilled water saturated under vacuum for 24 hours prior to testing.

A disk specimen was installed in a diffusion cell as illustrated in Fig. 2, with 1M and 0.1M KCl solutions on either side. Calomel reference electrodes were used to monitor the potential difference across the specimen. Chloride and potassium ions have similar self diffusion coefficients in water (1.85×10^{-9} and 1.87×10^{-9} m^2/s respectively in 0.5M solution at 25°C) and so any liquid junction potential would be negligible in the experimental set up. Hence the measured potential may be taken as a membrane potential.

After 10 days the solutions were replaced and the potential difference across the specimen was again monitored. The experiment was repeated with another specimen using sodium chloride solutions.

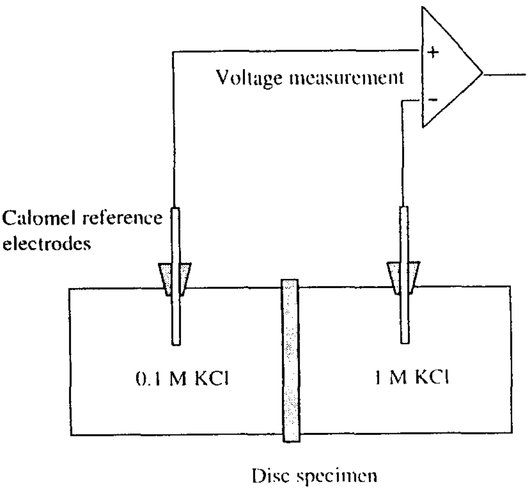

FIG. 2.
Membrane potential measurement set up.

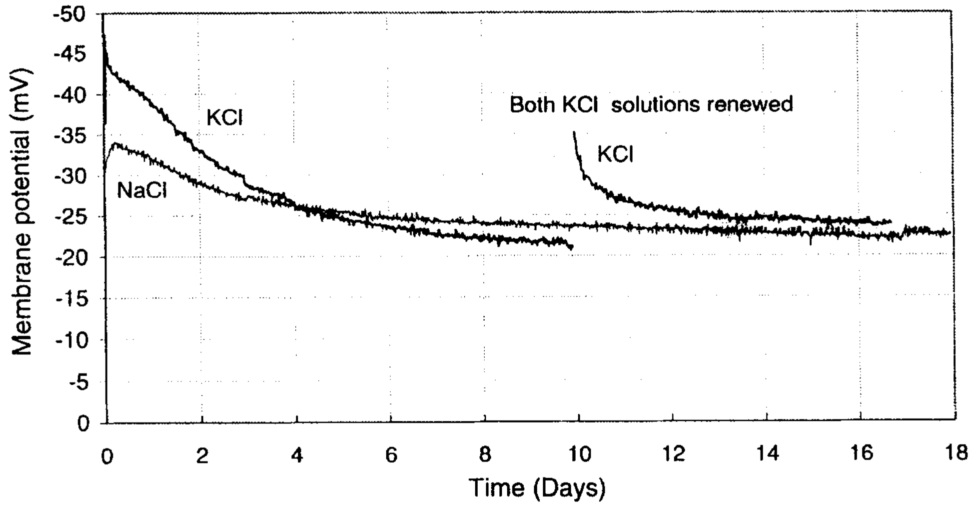

FIG. 3.
Variation in membrane potential with time across 10mm thick OPC mortar specimen.

Results

Fig. 3 presents the variation in membrane potential with time. An initial membrane potential of 45mV gradually reduced to around 21mV. When the solutions were replaced, the membrane potential increased to 35mV and then gradually reduced again. When the experiment was repeated with sodium chloride solutions the potential measured started at 34mV and gradually dropped to around 22mV after 18 days.

Discussion

The influence of electric fields of this magnitude on ion transport in cementitious materials is well established (16,17). Fig. 4 shows the effect of membrane potential on flux in a diffusion cell for different values of chloride ion diffusion coefficient, based on Eq. (2). It can be seen that the flux, and hence the calculated value of D_a, is very sensitive to membrane potential.

To model the effects of membrane potential on chloride transport, self diffusion coefficients are required. For pastes and mortars this involves retaining specimens in the diffusion cells, measuring steady state ion flux and then applying Eq.(4):

$$J = -D_a\frac{\partial C}{\partial x} = -D_s\frac{\partial C}{\partial x} - \frac{FZ}{RT}CD_s\frac{\partial \varphi}{\partial x} \qquad (4)$$

Fig. 5 shows the predicted effect of membrane potential on the chloride profile in concrete with a chloride diffusion coefficient of 4 x 10^{-12}m^2/s, making the simplifying assumption of no chloride binding. Again the effect is substantial and hence this self produced electric field is

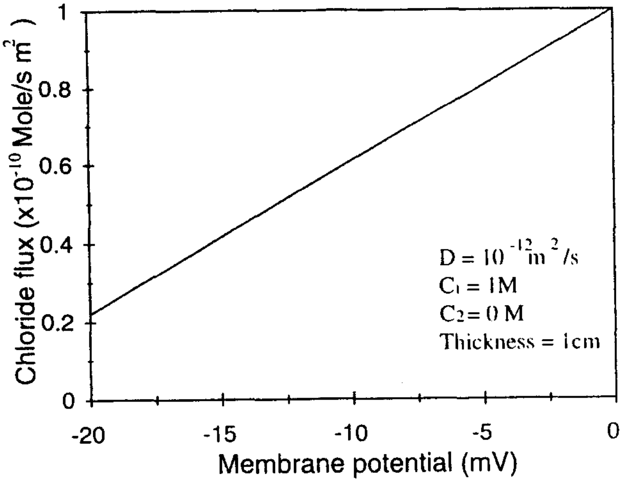

FIG. 4.
Effect of membrane potential on diffusion cell flux.

considered to be a crucial factor affecting chloride transport in concrete and is also likely to be important with respect to the transport of other ions, including sulfate.

The diffusion cell experiment was engineered to eliminate certain complicating factors. However, cement paste pore solution ions leaching out of the specimen into the external solutions and binding of chloride by cement hydrates considerably complicate behaviour in relation to the simple model of a membrane exposed to a binary electrolyte. Further work is planned to identify the influence of material and environmental parameters on membrane

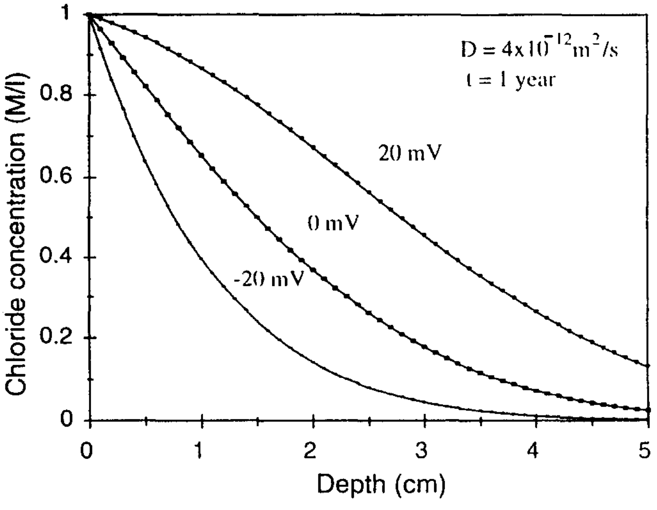

FIG. 5.
Effect of membrane potential on chloride profiles.

potential and its variation with time. By understanding the effect of cement and concrete parameters on membrane potential, it may also be possible to engineer materials to be particularly resistant to chloride penetration. An existing numerical (finite difference) model of chloride transport (18) will be extended to explicitly include the effect of membrane potential. This will then be used, together with the measured membrane potentials and self diffusion coefficients, to investigate the importance of membrane potential effects in practical situations involving chloride diffusion in concrete. Errors resulting from membrane potential effects involved in predicting long chloride profiles based on the results of short term tests will be studied. The existence of relatively large membrane potentials also has implications for chloride barrier and cathodic protection criteria, for assessing the performance of cathodic protection systems and for measuring corrosion potential of steel in concrete.

Conclusions

1. Membrane potentials of between 20 and 45mV have been measured across OPC mortar specimens housed in chloride diffusion cells. Although previous research has indicated the membrane nature of hardened cement paste, this is believed to be the first time that membrane potentials for cementitious materials have been measured and reported.
2. Electric fields of this magnitude have a significant effect on chloride ion transport in cementitious materials.
3. Further work is required to quantify the influence of concrete and environmental parameters on membrane potential and to establish if/how membrane potential effects should be taken into account in:
    - interpretation of chloride diffusion test results;
    - prediction of chloride profiles;
    - measurement and interpretation of reinforcing steel potentials; and
    - design of electrochemical chloride extraction and cathodic protection systems.

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