Cement & Concrete Composites 24 (2002) 451–455

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

Measurement and modelling of membrane potentials across OPC mortar specimens between 0.5 M NaCl and simulated pore solutions

J.-Z. Zhang [a,*], JianYun Li [b], N.R. Buenfeld [a]

[a] Department of Civil and Environmental Engineering, Imperial College, London SW7 2BU, UK
[b] China Building Materials Academy, Beijing 100024, PR China

Abstract

This paper reports experimental measurement and theoretical simulations of membrane potentials across OPC mortar specimens between 0.5 M NaCl and simulated pore solutions with various OH^- concentrations. The effect of OH^- counter transport and cation transport on membrane potentials is discussed. Membrane potentials are found to increase with an increase in OH^- concentration. Model simulations are consistent with the measured membrane potentials. This study confirms that cations diffuse much more slowly than anions and that OH^- ions diffuse significantly faster than Cl^- ions. Membrane potentials across OPC mortar specimens between NaCl and simulated pore solutions are mainly determined by OH^- and Cl^- transport. A simplified Henderson equation is recommended for membrane potential modelling of thin specimens in diffusion cell tests in which simulated pore solutions are used.

Keywords: Membrane potential; Ion transport; Modelling; Corrosion; Cement; Concrete

1. Introduction

Water saturated hardened cement pastes are porous materials containing a concentrated alkaline pore solution. When cement-based materials are exposed to a wet environment, ions in both the pore solution and the environmental solution transport within the material according to their concentration gradients. Because of the different mobility of the ions in a cementitious paste, the charge balance across the ion transport zone may not be maintained, resulting in an electrical field. This self established electrical field, in return, regulates ion transport to achieve electrical neutrality in the system. Consequently, ion transport becomes dependent on both the concentration gradient and the electrical field. The electrical field is characterised in terms of membrane potential [1]. The effect of membrane potential on ion transport has been found to be significant [2].

An early study indicated that OH^- counter diffusion may play an important role in determining membrane potentials and hence chloride transport [2]. The alkali content of different cement pastes varies significantly and this may be a factor affecting the resistance of different cement pastes to chloride diffusion. This work investigates the effect of the OH^- concentration of simulated pore solutions on membrane potentials across OPC mortar specimens.

It is recognized that cations diffuse much more slowly than anions in OPC pastes [3,4]. Therefore, it can be assumed that the transport behaviour of anions, particularly OH^- and Cl^- ions, largely determines ion transport properties of cement paste. While OH^- counter diffusion has been recognised as playing a part in Cl^- ion transport, the interaction has not been thoroughly investigated. It is normally assumed in chloride modelling that the diffusion coefficient ratio of OH^- and Cl^- ions in cement pastes, D^s_{OH}/D^s_{Cl}, is similar to that in water. However, a diffusion cell study showed that the ratio is much higher [2]. Therefore, this work also examines the value of D^s_{OH}/D^s_{Cl} and its effect on membrane potentials by theoretical simulations.

2. Experimental

2.1. Specimens

100 mm diameter, 50 mm thick OPC mortar discs were cast using 0.34 free water/cement, 2.5 sand/cement

---

[*] Corresponding author. Fax: +44-0207-594-6053.
E-mail address: j.zhang01@ic.ac.uk (J.-Z. Zhang).

0958-9465/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0958-9465(01)00076-2

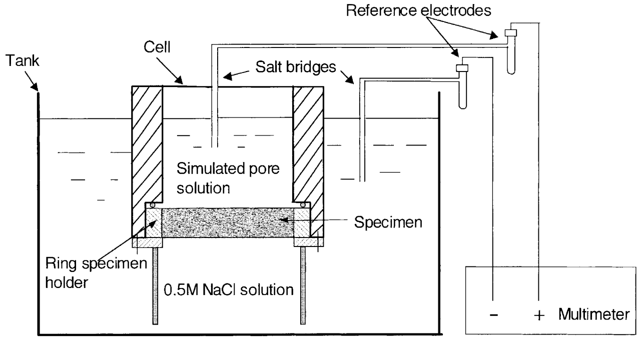

Fig. 1. Specimen and experimental set up.

and a maximum sand size of 2.36 mm. The fresh mortar was compacted for 3 min on a vibration table during casting. The specimens were demoulded after 2 days and were then stored in a sealed condition at 22 ± 2 °C to an age of 28 days. Prior to test, 10 mm thick, 100 mm diameter slices were cut from the centre of the discs. The curved surfaces of the specimens were coated with epoxy resin. Finally the specimens were sealed into ring specimen holders using silicone sealant and then were fitted into cells as shown in Fig. 1.

2.2. Test set up

As shown in Fig. 1, the specimens separated the cell solution and the solution in the tank. The cell solution had a volume of 0.5 l. Four cell solutions were selected as listed in Table 1. Solution 2 was formulated based on the pore press results of [5]. The other three cell solutions were prepared by proportionally reducing or increasing the KOH and NaOH contents based on solution 2 and then saturating with $Ca(OH)_2$. The tank solution was 44 l of 0.5 M NaCl solution. The relatively large volume of chloride solution ensured that its composition did not change significantly during a test while the small volume of the simulated pore solution enabled ions passing through the specimen to be present at detectable levels. The simulated pore solution represents infinite bulk concrete, providing pore solution ions to diffuse into the NaCl solution and prevents leaching from the upper face.

Before the cells were put into the tank, the specimens were conditioned for 3 days using simulated pore solution 2. The other sides of the specimens were exposed to open air during conditioning. Prior to installing the cells into the tanks, the conditioning cell solution was replaced with the appropriate cell solution. The tests using cell solution 2 were carried out in an early experiment and had the same mix and pre-conditioning as the other specimens used in the experiment. Three replicate specimens, installed in a single tank, were tested for each cell solution. The average result of three specimens is reported.

2.3. Membrane potential measurements

A detailed description of the membrane potential measurement method used was reported in [6]. Two identical calomel reference electrodes and salt bridges (made with Arga gel and saturated KNO_3 solution) were used as shown in Fig. 1 together with a multimeter with an input impedance of higher than 10^{10} Ω.

The potentials of the two reference electrodes were regularly checked to ensure that their potential difference in a KCl solution was less than 0.2 mV. To avoid contamination of test solutions with KNO_3 from the salt bridges, continuous membrane potential monitoring was not used. Salt bridges were only put into the test solutions when measurements were required. Normally the time to achieve a stable reading was no more than 5 min.

Considering the junction potentials involved:

$$\begin{aligned}\Delta\varphi_{\text{mem}} &= E_{\text{cell}} - (\varphi_2 - \varphi_1)\\ &= E_{\text{cell}} - [(\varphi_2^r + \varphi_{\text{junc2}}) - (\varphi_1^r + \varphi_{\text{junc1}})]\\ &= E_{\text{cell}} - (\varphi_{\text{junc2}} - \varphi_{\text{junc1}}) \qquad (1)\end{aligned}$$

where φ_2^r and φ_1^r are the standard potentials of the reference electrodes and are equal. Junction potentials φ_{junc1} and φ_{junc2} between the two salt bridges and the test solutions were estimated by the Henderson equation [7]:

$$\Delta\varphi_{\text{junc}} = \frac{RT}{F}\frac{(U_t - V_t) - (U_s - V_s)}{(U_t' - V_t') - (U_s' - V_s')}\ln\frac{U_t' - V_t'}{U_s' - V_s'}, \qquad (2)$$

where

$$U = \sum c_+ D_+^0, \quad V = \sum c_- D_-^0,$$
$$U' = \sum c_+ D_+^0 |Z^+|, \quad V' = \sum c_- D_-^0 |Z^-|,$$

Table 1
Solutions used in the tests

		Total OH^- (M)	KOH (M)	NaOH (M)	$Ca(OH)_2$
Cell solutions	1	0.10	0.072	0.028	Saturated
	2	0.23	0.16	0.065	
	3	0.50	0.35	0.14	
	4	0.70	0.50	0.20	
Tank solution		0.5 M NaCl			

where c is the molar concentration, Z is the valence of an ion, D° is the ion diffusion coefficient in a diluted solution. t and s denote test solution (i.e. chloride solution or simulated pore solution) and salt bridge solution, respectively, and + and − represent cations and anions, respectively.

Based on textbook ion diffusion coefficient values and Eq. (2), the total junction potentials $\varphi_{\mathrm{junc2}} - \varphi_{\mathrm{junc1}}$ for the four solution combinations (Table 1) are −0.8, −2.2, −4.5 and −5.9 mV, respectively. All the membrane potentials reported in this paper have had junction potentials subtracted using the estimated junction potential values and were measured against the reference electrode placed in the NaCl tank solution.

Eq. (2) is also used for membrane potential simulation in this work where D° is taken as the ion self-diffusion coefficient in hydrated cement paste.

3. Results

Fig. 2 shows membrane potentials measured using the four different cell solutions (with 0.5 M NaCl as the tank solution) over a period of 58 days. All membrane potentials measured were positive. The membrane potentials increased rapidly over the first few days, increasing more gradually thereafter. The membrane potentials on the 58th day are plotted in Fig. 2 as a function of OH^- concentration. The membrane potential increases with the increase in OH^- concentration, this effect being more marked at lower OH^- concentrations.

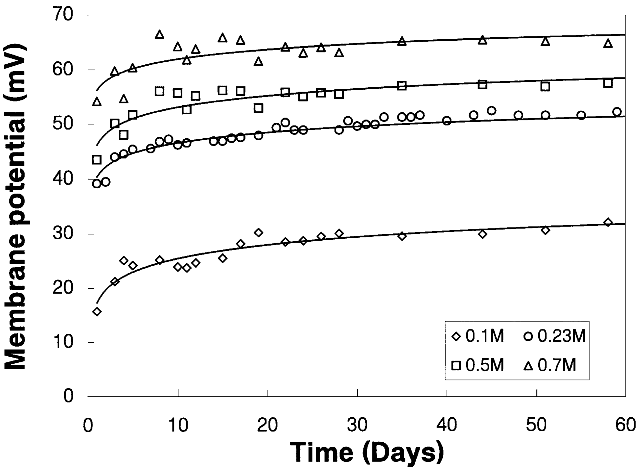

Fig. 2. Membrane potentials as a function of time.

4. Modelling of membrane potentials

For thin specimens tested in diffusion cell tests, membrane potentials can be modelled by the Henderson Eq. (2) if the self-diffusion coefficient of each ion involved is known. There are few published self-diffusion coefficient data for ions in cement paste. However, data from [3] are very useful because the techniques used in the study were interdiffusion and radioisotopic methods, which minimise osmotic and membrane potential effects. Therefore, the intrinsic diffusion coefficient measured in the tests should be close to the self-diffusion coefficient. The self-diffusion coefficients of Cl^- and Na^+ are assumed to be similar to those of B_r^- and C_s^+, respectively, in hydrated cement pastes and their values can be estimated from the data in [3]. Hence, for $w/c = 0.34$, D^s_{Cl} and D^s_{K} are estimated as 2.2×10^{-12} and 0.26×10^{-12} $\mathrm{m^2/s}$, respectively. D^s_{K} is arbitrarily taken equal to D^s_{Na} in most of the simulations. In an earlier study, D^s_{OH} was measured to be 7.5 times D^s_{Cl} in mortar specimens with a free w/c ratio of 0.4 [2]; $D^s_{\mathrm{OH}}/D^s_{\mathrm{Cl}}$ ratios of 7.5, 10 and 12 are used in the simulations presented here.

The simulations were designed to examine the effects of activity coefficient, cation diffusion coefficients and $D^s_{\mathrm{OH}}/D^s_{\mathrm{Cl}}$ ratio on membrane potentials by varying their input values. The average activity coefficients, $\gamma_\pm$, of the electrolytes can be found in [8] as 0.68, 0.78, 0.74, 0.71 and 0.72 for 0.5 M NaCl and cell solutions 1, 2, 3 and 4, respectively. The effect of Na^+ concentration in the cell solution on the activity coefficient is neglected as its concentration is relatively low. The values of the input parameters are listed in Table 2.

Simulation results are presented in Fig. 3. All the simulations show a very similar trend to the experimental results with membrane potential increasing with an increase in OH^- concentration.

Simulation 1 does not take account of the effect of activity coefficient. Comparison of Simulations 1 and 2 shows that the activity coefficient effect is minimal

Table 2
Inputs for membrane potential simulations

	$D^s_{\mathrm{OH}}/D^s_{\mathrm{Cl}}$	D^s_{K}, D^s_{Na} ($\mathrm{m^2/s}$).	$\gamma_\pm$	Note
Simulation 1	7.5	$D^s_{\mathrm{K}} = D^s_{\mathrm{Na}}$	1 (all solutions)	$D^s_{\mathrm{Na}} = 0.26 \times 10^{-12}$ ($\mathrm{m^2/s}$)
Simulation 2	7.5	$D^s_{\mathrm{K}} = D^s_{\mathrm{Na}}$	0.72 (0.5 M NaCl)	(except simulation 4),
Simulation 3	7.5	$D^s_{\mathrm{K}} = 2 \times D^s_{\mathrm{Na}}$	0.68 (solution 1)	$D^s_{\mathrm{Cl}} = 2.2 \times 10^{-12}$ ($\mathrm{m^2/s}$).
Simulation 4	7.5	$D^s_{\mathrm{K}} = D^s_{\mathrm{Na}} = 0$	0.78 (solution 2)	
Simulation 5	10	$D^s_{\mathrm{K}} = D^s_{\mathrm{Na}}$	0.74 (solution 3)	
Simulation 6	12	$D^s_{\mathrm{K}} = D^s_{\mathrm{Na}}$	0.72 (solution 4)	

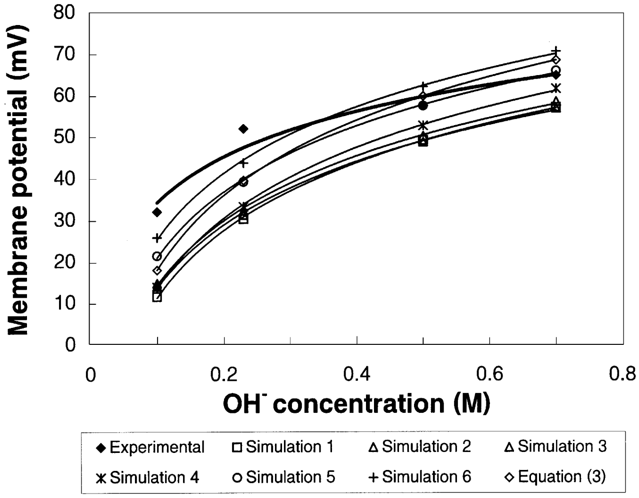

Fig. 3. Membrane potential simulation results.

except at low concentrations. This is because, as far as the tests in this work are concerned, the activity coefficient does not vary much over the concentration range and it has a similar effect on both the cell solutions and the tank solution. When the concentration of the simulated pore solution is low the activity coefficient increases, resulting in a higher membrane potential. Simulations 2–4 show no significant changes in membrane potential when the self-diffusion coefficients of K^+ and Na^+ vary. The reasons are that the anion diffusion coefficients are very low in comparison to those of chloride ion and hydroxyl ions and both solutions contain K^+ and Na^+ and they partially offset each other. The insignificant effect of cations on membrane potential also justifies the approximation of D^s_K and D^s_{Na} in the simulations. Simulations 2, 5 and 6 clearly indicate that D^s_{OH}/D^s_{Cl} is the main factor affecting membrane potential in the system tested. From the results, the actual D^s_{OH}/D^s_{Cl} is estimated to be around 10 and possibly as high as 12 in the cement paste. This ratio is far higher than that in water, consistent with the high experimental D^s_{OH}/D^s_{Cl} value (7.5) reported in [2].

The simulations confirm (1) that cations diffuse much more slowly than anions in cement paste; (2) that hydroxyl ions diffuse much faster than chloride ions and (3) that the membrane potential of a specimen between pore solution and a NaCl solution is mainly determined by D^s_{OH}/D^s_{Cl} and c_{OH}/c_{Cl} ratios.

5. Discussion

5.1. Cation transport and its effect on membrane potential

The membrane potential results confirm that cations diffuse much more slowly than anions in cementitious materials. Early membrane potential measurements on diffusion cells using de-ionised water instead of simulated pore solution gave negative membrane potentials [2]. This indicates that, without OH^- counter transport, membrane potential is mainly determined by the difference in self-diffusion coefficients of Cl^- and Na^+ ions. The absolute value of the negative membrane potential is higher than that estimated from the diffusion coefficient ratio of Cl^- and Na^+ in water. For OPC mortars with a free *w*/*c* ratio 0.4, the measured membrane potential is about −20 to −25 mV between 0.1 M and 1 M NaCl solutions [1]. The estimated membrane potential of such a system based on the diffusion coefficient ratio of Cl^- and Na^+ in water yields a value of about −12 mV. The low cation self-diffusion coefficient is further demonstrated in the simulations. Simulations 2, 3 and 4 show little effect on membrane potentials of varying the cation diffusion coefficient value. The slow cation transport has two implications: (1) in the absence of OH^- counter transport (or where OH^- concentration is very low compared to NaCl concentration), NaCl transport into a specimen produces a negative membrane potential due to the difference in self-diffusion coefficient of Cl^- and Na^+ ; and (2) where OH^- and Cl^- are counter diffusing, cation transport has a minimal effect on the membrane potential of the system.

5.2. Effect of OH^- and Cl^- transport on membrane potential

Both the experimental and simulation results show a high D^s_{OH}. The result in this study is fully supported by the early direct measurement of hydroxyl diffusion [2]. Simulations 5 and 6 using high D^s_{OH}/D^s_{Cl} ratios fit the experimental results better than when lower values are used. As a result of high D^s_{OH}, a positive membrane potential was measured even when the OH^- concentration was as low as 0.1 M. The results indicate that the ratio of OH^- and Cl^- self-diffusion coefficients could be as high as 12 in the system studied.

5.3. Simulation of membrane potential

Simulations 5 and 6, using $D^s_{OH}/D^s_{Cl} = 10$ and 12, respectively, give reasonable predictions of the experimental values. The large deviations at low concentrations are possibly caused by the following two factors: (1) the membrane potentials at the 0.23 M OH^- concentration were measured in a separate experiment and were relatively high in comparison to the values at other concentrations; (2) the membrane potentials at the low OH^- concentrations might be affected by the back diffusion of OH^- ions from the real pore solution in the specimens into the simulated pore solution, shifting membrane potential in the positive direction. Considering these factors, simulation 5 is taken as the more reasonable prediction.

The simulations show that the membrane potentials are mainly controlled by $D^{\mathrm{s}}_{\mathrm{OH}}/D^{\mathrm{s}}_{\mathrm{Cl}}$ ratios. Therefore, the Henderson equation can be simplified to

$$\Delta\varphi_{\mathrm{mem}} = \frac{RT}{F}\ln\left(\frac{c_{\mathrm{OH}}D^{\mathrm{s}}_{\mathrm{OH}}}{c_{\mathrm{Cl}}D^{\mathrm{s}}_{\mathrm{Cl}}}\right). \quad (3)$$

Calculated membrane potential results from Eq. (3) using a $D^{\mathrm{s}}_{\mathrm{OH}}/D^{\mathrm{s}}_{\mathrm{Cl}}$ ratio of 10 are also plotted in Fig. 3. It is clear that the results calculated from Eq. (3) are very close to those predicted using Eq. (2).

There are a number of factors limiting the accuracy of membrane potential prediction by Eq. (2) or (3). First, the approach for membrane potential modelling used in this work is a simple thermodynamic method that treats the cement specimen as a homogeneous material. A more complex model could take account of the effects of the pore structure, electrical double layer and ionic interactions but would require determination of a large number of solution chemistry parameters for the cement system in question. Second, the input parameters, for example the diffusion coefficients, used in the modelling are based on the literature and are likely different from their real values in the system studied in this particular work. Furthermore, use of individual ion activity coefficients might be better than the average ones used in the modelling because hydrated cement is a multi-ionic system.

6. Conclusions

The effects of OH^- transport on the membrane potentials established across OPC mortar specimens in diffusion cell tests have been experimentally studied. Increasing OH^- counter transport to Cl^- raises the membrane potential. Theoretical simulation of membrane potentials using the Henderson equation and existing experimental diffusion coefficient data yields fair estimations of measured values. For the pore solution/specimen/NaCl system studied in this work, a simplified Henderson equation is recommended. Comparison of theoretical simulations with experimental results for OPC mortar specimens confirms that (1) cation transport is slower than anion transport and has little effect on the membrane potential measured across a specimen separating NaCl and alkaline solutions; (2) OH^- ions diffuse about 10 times faster than Cl^- ions; and (3) the membrane potential across a specimen separating NaCl and alkaline solutions is primarily controlled by OH^- and Cl^- self-diffusion coefficient and concentration ratios.

References

[1] Zhang J-Z, Buenfeld NR. Presence and possible implications of membrane potential in concrete exposed to chloride solution. Cem Concr Res 1997;27(6):853–9.

[2] Zhang J-Z, Buenfeld NR. Membrane potential and its influence on chloride transport in cementitious materials. In: Andrade C, Kropp J, editors. Proceedings of the 2nd International RILEM Workshop on Testing and Modelling Chloride Ingress into Concrete. Paris: RILEM publications 2000;33–50.

[3] Atkinson A, Nickerson AK. The diffusion of ions through water-saturated cement. J Mater Sci 1984;19:3068–78.

[4] Goto S, Roy DM. Diffusion of ions through hardened cement pastes. Cem Concr Res 1981;11:751–7.

[5] Andersson K, Allard B, Bengtsson M, Magnusson B. Chemical composition of cement pore solutions. Cem Concr Res 1989; 19(3):327–32.

[6] Zhang J-Z, Buenfeld NR. Measuring the membrane potential across cementitious materials. Mater Struct 2000;33:492–8.

[7] Bates RG. Determination of pH – Theory and Practice. New York: Wiley; 1964.

[8] Robinson RA, Stokes RH. Electrolyte Solutions. 2nd ed. London, Butterworths: Scientific Publications; 1959.