Pergamon

Cement and Concrete Research 31 (2001) 621–625

CEMENT AND CONCRETE RESEARCH

Oxygen and chloride diffusion in cement pastes as a validation of chloride diffusion coefficients obtained by steady-state migration tests

M. Castellote[a],*, C. Alonso[a], C. Andrade[a], G.A. Chadbourn[b],
C.L. Page[c]

[a]Institute of Construction Science "Eduardo Torroja', CSIC, 28033 Madrid, Spain
[b]Department of Civil Engineering, Aston University, Birmingham, UK
[c]School of Civil Engineering, University of Leeds, Leeds, UK

Received 31 May 2000; accepted 29 January 2001

Abstract

When chloride ions diffuse through concrete, it has been found that they interact with the surface charge and electrical double layer developed at the cementitious matrix/pore solution interface. As a consequence of this interaction, the diffusion of chloride ions is retarded in comparison with that of dissolved oxygen molecules, although the two species have very similar diffusion coefficients in infinitely aqueous dilute solutions. This is taken to imply that electrostatic, rather than purely steric, factors limit the ability of chloride ions to diffuse through pores below a critical radius. If an electrical field is applied to accelerate chloride transport through concrete, it is uncertain what effect this may have on the size range of pores that are accessible to the migrating ions. At high applied voltages, it might even be that the normal electrostatic interactions that influence ionic diffusion are nullified so that chloride ions can traverse pores of similar radii to those that are accessible to dissolved oxygen. This would be expected to give rise to an apparent increase in the value of 'diffusion coefficient' obtained for chloride. To investigate whether, during a steady-state migration test, chloride ions diffuse through the essentially the same range of pores as during a natural steady-state diffusion test, experimental studies (oxygen diffusion, natural diffusion and migration tests) have been carried out with a limited range of cement pastes. The results indicate that, at the recommended applied voltage (12 V) and for cementitious materials of the type studied, steady-state migration tests can be used to determine 'effective diffusion coefficients' that are of similar magnitude to those obtainable from natural steady-state diffusion measurements.

Keywords: Oxygen diffusion; Chloride migration; Chloride diffusion; Steady-state tests

1. Introduction

The rapid determination of chloride 'diffusion coefficients' from migration tests is extending and becoming a common practice. Although theoretically, the feasibility of the approach has been established, experimentally, there are still many points that remain to be clarified. One of the main uncertainties arises because it has not been established whether the application of electrical fields to concrete alters the nature and significance of surface interactions that take place between chloride ions and the cement matrix. If such effects were produced, 'diffusion coefficients' obtained from migration tests would not be representative of those calculated in natural diffusion conditions.

Several researchers have established that the surface of the particles of CSH gel are negatively charged, implying that an electrical double layer exists in the vicinity of the walls of pores [1–3]. Nowadays, it is accepted that ionic diffusion rates in hydrated cement pastes are greatly affected by the existence of this surface charge and double-layer region of the aqueous pore liquid phase [4–7].

In infinitely dilute aqueous solutions, the diffusion coefficients of chloride ions and dissolved oxygen molecules have quite similar values. This is not generally the case, however, in hydrated cement pastes of fine pore structure as

---

* Corresponding author. Tel.: +34-91-3020440 loc. 286; fax: +34-91-3020700.

E-mail address: martaca@fresno.csic.es (M. Castellote).

PII: S0008-8846(01)00469-0

oxygen is a neutral molecule without dipolar character whose diffusion within the pore solution phase cannot be influenced by electrostatic surface interactions of the kind that may affect the transport of chloride ions. Thus, the ratio of the effective diffusion coefficients of oxygen and chloride provides a measure of the extent to which electrostatic surface effects govern chloride transport in different types of cementitious matrix [8,9].

The aim of the present paper was to determine whether the acceleration experienced by chloride ions, as a consequence of an applied electrical field of a magnitude typically used in migration tests, would substantially affect the interactions between the matrix and the chloride ions. If the strength of the electrical field during the migration tests were sufficient to nullify the electrostatic interactions between moving ions and pore walls, it would imply an increase in the values of the effective 'diffusion coefficients' for chloride obtained by migration tests. In this case, the values obtained would be expected to tend towards those for dissolved oxygen molecules. To examine this possibility, comparative tests of steady-state transport of chloride ions by diffusion and migration, as well as measurements of steady-state oxygen diffusion have been performed through cement pastes of well-defined composition.

2. Experimental procedure

2.1. Materials and procedures

Paste specimens of Ordinary Portland cement (see composition in Table 1) were cast at a water/cement ratio of 0.4. After demoulding of the pastes and curing for 28 days under water, they were stored for 1 month immersed in a saturated $Ca(OH)_2$ solution.

All the specimens cast were cylindrical. Those for *natural diffusion* (chlorides and oxygen) were 49 mm in diameter and 75 mm in length. They were cut into discs of approximately 3 mm in thickness to provide samples for the steady-state diffusion tests.

Specimens prepared for *migration tests* were 75 mm in diameter and 150 mm in length, being cut into discs of approximately 10 mm in thickness to provide samples for testing in a migration cell, as described in Ref. [10]. The disc of paste separated two chambers where a cathode and an anode were placed. Two corrugated rebars, each 10 cm in length and 0.6 cm in diameter, were used as electrodes. Distilled water was introduced into the compartment where the anode was located (anolyte) and 1 M NaCl solution was used as catholyte. A potential difference of 12 V was applied between electrodes. Periodically during the experiment, the chloride ion concentration in both compartments was monitored by removing small volumes of the solution and analysing them by potentiometric titration with $AgNO_3$.

Natural chloride diffusion tests were carried out at 25°C in the usual two-compartment cell and according to the procedures described elsewhere [4]. The high concentration side of the diffusion cell contained saturated lime water in 1 M NaCl, while the low concentration side contained initially pure lime water in three of the cells. In the two other cells, instead of lime water, distilled water was used. In the same way as for migration tests, liquid samples were taken and the Cl^- concentration was analysed. In this case, the method of analysis was a standard spectrophotometric technique.

Natural oxygen diffusion tests were carried out at 25°C according to the technique described in Ref. [8] using glass diffusion cells. The anode compartment was filled with lime water through which a stream of oxygen was passed continuously, while the cathode compartment was filled with deaerated lime water. The anode was made from electrocatalytically activated titanium and the cathode from platinum. A saturated calomel electrode (SCE) was placed in the anode compartment. After diffusion of oxygen had proceeded for periods of about 2 days, the cathode was polarised at a potential of -0.6 V with respect to the SCE for a period of 15,000 s. The amount of diffused oxygen electrochemically consumed was obtained from the integrated charge passed.

2.2. Calculation of the diffusion coefficients

2.2.1. Migration tests

The calculations of the 'diffusion coefficients', from migration tests, were made using the modified Nernst–Planck equation [Eq. (1)] [10].

$$D_{\mathrm{ef}} = \frac{J_{\mathrm{Cl}} R T l}{z F C_1 \gamma \Delta\Phi} \tag{1}$$

where J_{Cl} is the flux of chlorides (mol/cm^2 s), C_1 the Cl^- concentration in the catholyte (mol/cm^3), γ the activity coefficient of the catholyte solution, l the thickness of the specimen (cm). $\Delta\Phi$ the effective voltage applied (V) and D_{ef} the effective diffusion coefficient (cm^2/s).

Table 1
Chemical analysis of the cement used

Component (%)									
Ignition loss	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Free CaO	Cl^-
3.45	1.97	19.37	6.12	3.13	62.86	1.78	3.23	1.28	0.013

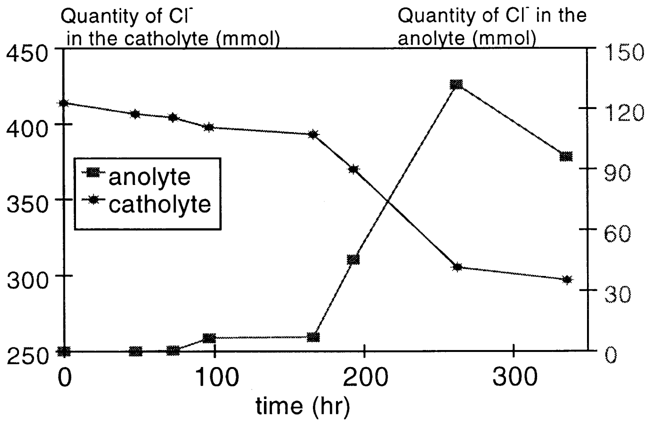


Fig. 1. Evolution in the amount of chloride in anodic and cathodic compartments.

2.2.2. Natural diffusion tests

From natural chloride diffusion tests, effective chloride diffusion coefficients were calculated according to Fick's First law [Eq. (2)].

$$\ln(C_1\gamma - C_2) = -\frac{D_{\mathrm{ef}}A}{Vl}(\Delta t) + \ln(C_1\gamma) \tag{2}$$

where C_1 is the Cl^- concentration in the source compartment (mol/cm^3), γ the activity coefficient of the solution in the source compartment, C_2 the Cl^- concentration in initially chloride-free compartment (mol/cm^3), V the volume of the initially chloride-free compartment (cm^3), Δt the diffusion time (s) and A the diffusion area (cm^2).

As mentioned, effective diffusion coefficients of dissolved oxygen through cement pastes were determined by the method described by Yu and Page [8], which is based on Fick's First law and Faraday's law according to the Eq. (3) [8].

$$J_{\mathrm{o}} = \frac{1000Q}{nF\Delta t} \approx \frac{D_{\mathrm{ef}}AC_{\mathrm{o}}}{l} \tag{3}$$

where J_{o} is the flux of oxygen (mmol/s), Q the charge passed (C), n the number of electrons transferred per molecule of oxygen and C_{o} the oxygen concentration (mol/l).

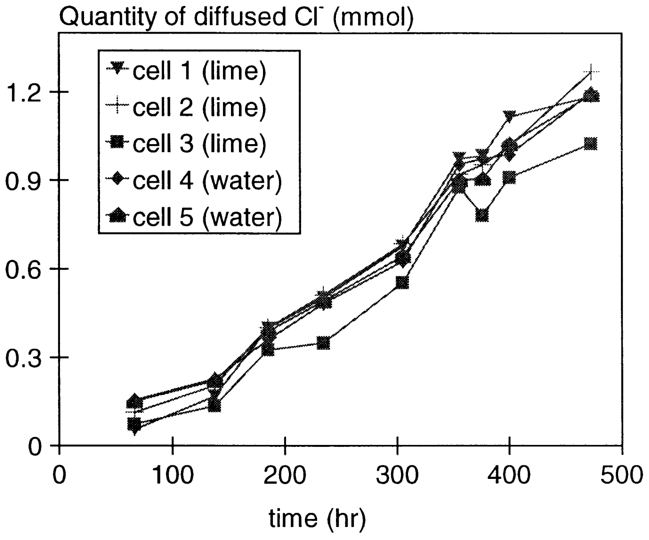


Fig. 2. Evolution in the amount of chlorides that have diffused through the specimen to reach the initially chloride-free compartment.

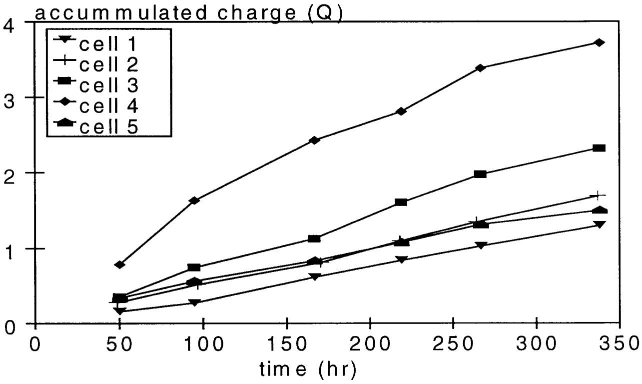


Fig. 3. Evolution in the accumulated charge as a function of diffusion time.

3. Results

Fig. 1 shows the results obtained from migration tests, the evolution in the accumulated amounts of chloride ions in both anodic and cathodic compartments being presented as a function of time.

It can be seen from the figure that the amount of chlorides passing to the anolyte evolves in three stages. Initially, there is a period in which the amount of chlorides that passes to the anolyte is negligible. Its duration corresponds to the so-called "time lag", which can be taken as the time required for chlorides to pass through the disc. After this stage, there is a "steady-state" period, in

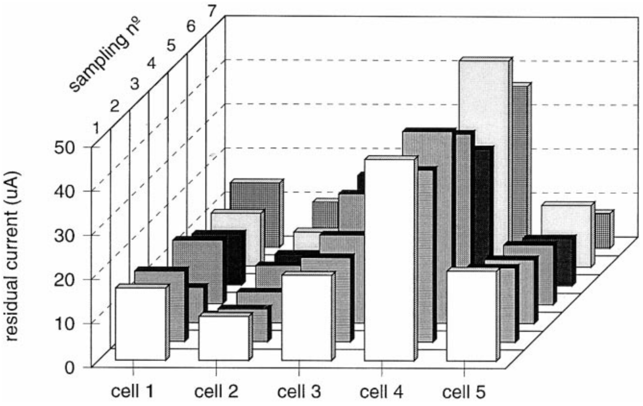


Fig. 4. Residual current values after the cathodic consumption of the oxygen.

which the flux of chloride ions through the specimen is practically constant and this allows the calculation of an effective “diffusion coefficient”. As far as the catholyte chloride level is concerned, the curve recorded presents a decreasing trend.

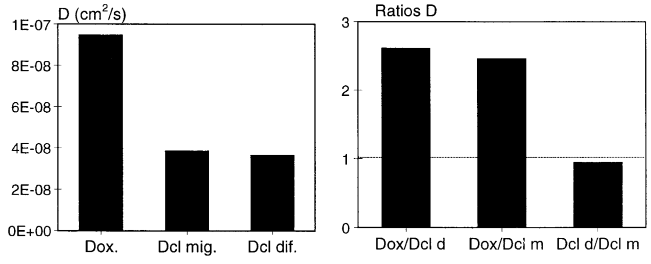
The results corresponding to the chloride diffusion experiments are presented in Fig. 2, where the total amount of chlorides that have diffused through the specimen to reach the low concentration compartment are shown. As has been mentioned, this kind of test was performed with two different kinds of initial solutions (0.3 M NaOH, and distilled water) in order to determine the influence of this parameter. As can be seen in Fig. 2, the outline of the curves corresponding to different tests were essentially the same, with no apparent differences between the cells whose solutions were of NaOH (numbers 1, 2 and 3) or distilled water (4 and 5).

Results corresponding to the oxygen diffusion test are presented in Fig. 3, where the accumulated charge corresponding to the different times at which cathodic reduction of the oxygen was carried out, is depicted. As can be seen, there is a rectilinear dependence of accumulated charge (and therefore of accumulated oxygen) on time, implying a steady flux of oxygen.

It is relevant to point out that for one of the cells (number 4), the total circulated charge values are higher than those corresponding to the other cells. The current values registered when all the oxygen has been reduced (after 15 000 s) in the cathodic compartment are so-called residual currents. Residual currents for these tests can be seen in Fig. 4, where it is clear that again values registered for cell number 4 are well above the others. This was probably due to the presence of a small crack in disc number 4, so the results corresponding to this cell have been ignored for the subsequent calculations.

3.1. Calculation of the diffusion coefficients

Effective diffusion coefficients calculated, according to Eqs. (1)–(3), are presented in Fig. 5a and b, where it can be seen that the coefficient corresponding to the oxygen molecule is clearly higher than those calculated for chloride, irrespective of the kind of test performed. In Fig. 5b, the ratio of the oxygen diffusion coefficient and the chloride diffusion coefficient has also been represented, following the approach established in Refs. [8,9], as it represents a numerical measure of the effect of the surface charge on chloride diffusion.



a) effective diffusion coeffients

b) ratio between coefficients

Fig. 5. (a–b) Comparison between chloride diffusion coefficients (from diffusion and migration tests) and oxygen diffusion coefficient.

4. Discussion

The results indicate that effective diffusion coefficients for chloride ions in Portland cement paste of fixed composition (w/c 0.4), obtained from steady-state natural diffusion and migration tests, are very similar (see Fig. 5). The values recorded for the effective diffusion coefficient of oxygen through the same material were clearly two to three times higher. This is in good agreement with the previous ratios of oxygen and chloride diffusion coefficients determined for Ordinary Portland cement pastes of similar composition to those studied in the present investigations [8,9].

This strongly suggests that, for specimens of the kind investigated, migration of chloride ions occurs in a similar way and through pores of essentially the same size range as those that are involved in the case of natural diffusion. Hence, the acceleration of the chloride ions produced by the electrical field, at the level applied in this study (ca. 10 V/cm), does not appear to alter their electrostatic interactions with the surface of the pores substantially. Steady-state migration tests of the kind described elsewhere [10] can therefore be used with reasonable confidence to obtain rapid estimates of “diffusion coefficients” of chloride ions in hydrated cement pastes of the type studied.

Further work would be useful in this field to assess how far it is possible to generalise the above findings. In particular, it would be interesting to evaluate the performance of cementitious binders incorporating ground granulated blast furnace slag, fly ash, microsilica and metakaolin as these materials can produce substantial refinement of the pore structures of hydrated cement pastes. This has been shown to result in ratios of effective diffusion coefficients for oxygen and chloride that far exceed those recorded for Portland cement paste of w/c 0.4 [8,9].

5. Conclusions

The results presented are believed to clarify a small part of the existing uncertainties concerning possible alterations in the complex interactions that take place between moving chloride ions and the cement matrix when an electrical field is applied to accelerate their transport. Thus, it appears that an applied electrical field (of magnitude typically used for migration testing) does not substantially distort the effect of the cement matrix surface charge on chloride diffusion. Hence, reliable estimates of effective "diffusion coefficients" of chloride ions in cement pastes of the type studied may be determined by appropriate steady-state migration tests.

References

[1] H. Londiche, F. Lancelot, Les phénomènes électrocinétiques et leurs aplications aux écoulements dans les milieux poreux, Ann Mines, Mai-Juin, (1984) 103–108.

[2] E. Nägele, The zeta-potential of cement: Part III. The non-equilibrium double layer on cement, Cem. Concr. Res. 17 (4) (1987) 573–580.

[3] S. Chatterji, M. Kawamura, Electrical double layer, ion transport and reactions in hardened cement paste, Cem. Concr. Res. 22 (5) (1992) 774–782.

[4] C.L. Page, N.R. Short, A. Tarras, Diffusion of chloride ions in hardened cement pastes, Cem. Concr. Res. 11 (3) (1981) 395–406.

[5] S. Goto, D.M. Roy, Diffusion of ions through hardened cement pastes, Cem. Concr. Res. 11 (1981) 751–757.

[6] U. Uchikawa, Proceedings of the 8th International Congress on Chemistry of Cement, Río de Janeiro, Brasil Abla SráJiec e Editora Ltda., Rio de Janeiro, Brasil 1 (1986) 249–280.

[7] S. Goto, M. Daimon, Proceedings of the 8th International Congress on Chemistry of Cement, Río de Janeiro, Brasil Abla SráJiec e Editora Ltda., Rio de Janeiro, Brasil 6 (1986) 405–409.

[8] S.W. Yu, C.L. Page, Diffusion in cementitious materials: I. Comparative study of chloride and oxygen diffusion in hydrated cement pastes, Cem. Concr. Res. 21 (1991) 581–588.

[9] V.T. Ngala, C.L. Page, L.J. Parrott, S.W. Yu, Diffusion in cementitius materials: II. Further investigations of chloride and oxigen diffusion in well cured OPC and OPC/30% PFA pastes, Cem. Concr. Res. 25 (4) (1995) 819–826.

[10] C. Andrade, Calculation of chloride diffusion coefficients in concrete from ionic migration measurements, Cem. Concr. Res. 23 (3) (1993) 724–742.