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Kinetics of oxygen diffusion in hardened cement pastes

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An electrochemical cell has been devised for measurement of the effective diffusivity of oxygen in water-saturated hardened cement pastes. The technique has been applied to investigate oxygen diffusion kinetics over the temperature range 15 to 35° C for Portland cement pastes of constant mineralogy but variable water–cement ratio. The values obtained for effective diffusivity and activation energy have been compared with previously published kinetic data for ionic diffusion in similar materials. Implications regarding the electrochemical behaviour of steel embedded in water-saturated cement matrices have also been examined with particular reference to prediction of limiting conditions of oxygen supply governing the transition from a state of passivity, characterized by a stable film of Fe_2O_3, to one of general dissolution, associated with a stable alkali-soluble species, $Fe(OH)_3^-$.

1. Introduction

Steel embedded in concrete or cement grout is usually in a state of passivity, being protected from significant corrosion by a surface film of Fe_2O_3. The latter is thermodynamically stable in an alkaline medium such as cement pore liquid (typically pH 13 to 14) over a wide range of rest potentials corresponding to environments of varying redox tendency [1]. There are two fairly common circumstances that may give rise to breakdown of this passive film, (a) carbonation, which depresses the pH towards neutral values rendering Fe_2O_3 unstable, and (b) the presence of chloride salts, which may stimulate local disruption of the film leading to pitting corrosion [2].

A third mechanism of depassivation can, however, be encountered under conditions of exposure such as exist in certain buried or submerged situations where oxygen availability is very low. Here the maximum rate of the diffusion-controlled cathodic process ($O_2 + 2H_2O + 4e^- = 4OH^-$) may be insufficient to balance the anodic "leakage" current density required to maintain a passive film and a form of behaviour known as "active low-potential corrosion" or "cathodically restrained general dissolution" becomes established. In this state, the film-free metal surface attains a rest potential less noble than about −850 mV (SCE scale) and undergoes uniform anodic dissolution at a very low rate, controlled by the diffusional flux of cathodic reactant [3, 4]. Whilst corrosion rates associated with this condition are generally insignificant, they require consideration in circumstances where abnormally long service-life is envisaged, e.g. in applications related to the containment of buried radioactive wastes. It is necessary also to be able to predict whether embedded steel will exhibit active, low potential behaviour or passivity, with characteristically noble potential, in structures such as offshore concrete platforms where galvanic interactions between reinforcement and externally exposed steelwork are likely to occur.

The two critical parameters that must be known for the electrochemical state of steel in concrete or cement grout to be predicted under conditions of low oxygen concentration and water saturation are:

(i) the anodic leakage current density to maintain the passive film on steel in contact with the cement matrix, and

(ii) the limiting diffusion current density for cathodic reduction of oxygen.

Whilst measurements of the first of these parameters [5] have yielded values (in the range, 0.1 to 1 $mA\,m^{-2}$) in good agreement with independently determined corrosion current densities for passive steel in cement matrices [6], data regarding the kinetics of oxygen diffusion are extremely confusing when results of different workers are compared. Diffusion coefficients quoted for oxygen in saturated concretes have ranged from larger than 10^{-6} to about $10^{-9}\,cm^2\,sec^{-1}$ and it remains unclear whether the wide variations recorded are ascribable mainly to differences in materials, specimen preparation or measurement techniques [7–9].

It was, therefore, considered that a study of oxygen diffusion kinetics in saturated cement pastes would be of interest, particularly if made using well-characterized specimens of the sort that have been employed for previous investigations of ionic diffusion kinetics [10]. The influences of variables such as water/cement ratio and temperature (over a limited range) on the effective diffusion coefficients for chloride ions in hardened cement pastes are reasonably well established [10–12] and a specific aim of the present study was thus to compare the effects of these same variables on the kinetics of oxygen diffusion.

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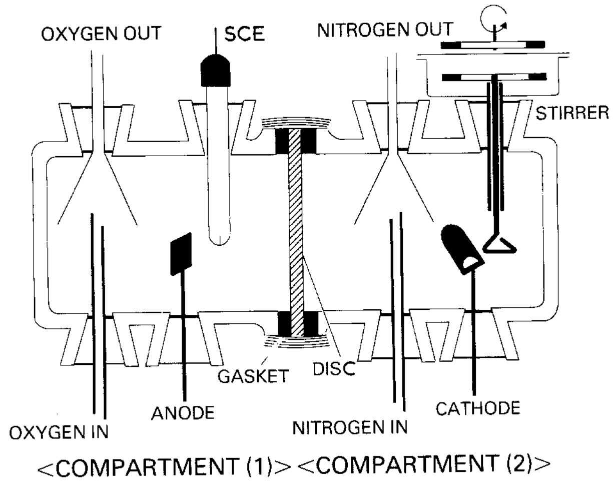

Figure 1 Electrochemical cell for measurement of oxygen diffusivity.

2. Experimental procedure

Measurements of the effective diffusivity of oxygen in hardened cement pastes were performed in a glass cell of the kind illustrated in Fig. 1, which was similar in scale to those used in previous work on chloride diffusion [10]. The cell consisted of two compartments separated by a disc of cement paste of thickness 2 to 2.5 mm, and diameter 50 mm. The electrolyte in both compartments was saturated $Ca(OH)_2$ solution, chosen to avoid leaching of hydration products from the cement paste.

The discs were cut from cylinders of Ordinary Portland cement pastes, prepared as described previously [10] and cured for 60 days at 20° C in sealed moulds. The cement analysis was as shown in Table I and the water/cement ratios of the pastes studied were 0.4, 0.5 and 0.6, as in earlier investigations [10]. After being cut and lightly ground on 600 grade emery paper, the discs were stored under saturated $Ca(OH)_2$ for a further period of up to 4 days before being mounted in the diffusion cell with the aid of neoprene rubber gaskets and PTFE tape. The cell was then suspended in a thermostatically controlled water bath in which the temperature was maintained at 15, 25 or 35° C. The cell was fitted with a system of three electrodes, consisting of a platinized titanium anode and saturated calomel reference electrode (SCE) in compartment 1, with a platinized titanium cathode in compartment 2. Provision was made for 99.9% pure oxygen and nitrogen gases to be passed via glass frits through the solutions in compartments 1 and 2, respectively, and a magnetically coupled stirrer was rigidly mounted in compartment 2.

To carry out a measurement of the rate of oxygen diffusion through a disc, the solutions in compartments 1 and 2 were initially saturated with oxygen and nitrogen, respectively, by bubbling the gases through the cell for several hours. The nitrogen stream was then stopped but the oxygen stream was maintained so that diffusion caused the oxygen concentration of the solution in compartment 2 to rise progressively from an original value of effectively zero, with the solution in compartment 1 remaining oxygen-saturated throughout. After a suitable time had elapsed, in the range 18 to 48 h, the stirrer in compartment 2 was started and the cell electrodes were connected to an electronic potentiostat with current measurement and integration facilities (Princeton Applied Research, Model 350 Corrosion Measurement System). The cathode was then polarized to a potential of − 400 mV against SCE, at which the only significant reaction was expected to be the reduction of dissolved oxygen. This potential was maintained until the recorded current passing through the cell had decayed to a value close to zero, at which point the integrated charge passed was taken to represent the total quantity of oxygen that had reached compartment 2 by diffusion. A typical current/time trace is represented in Fig. 2.

TABLE I Analysis of OPC (wt %)

CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	Ignition loss
63.4	20.2	7.3	2.3	3.1	1.2	0.4	0.5	0.9

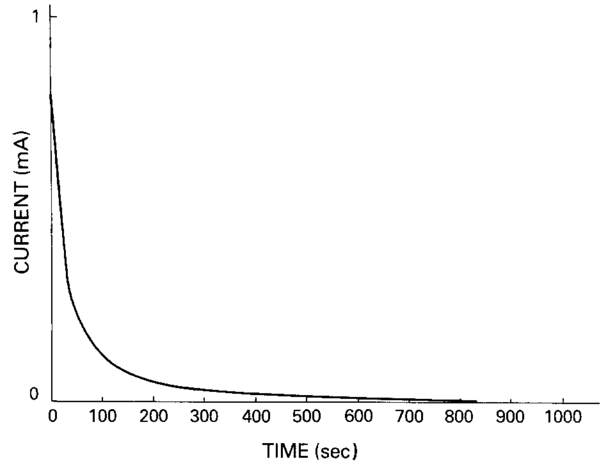

Figure 2 Typical current/time trace for reduction of oxygen.

Important features of the cell design were the efficiency of stirring within the cathode compartment and the relatively large size of the cathode itself ($\sim 10\,cm^2$). With this combination, it was possible to carry electrochemical reduction of the dissolved oxygen in compartment 2 virtually to completion within a maximum time of 15 min, which was considered negligible in comparison with the diffusion periods of 18 to 48 h. Ignoring the small capacitive effects of electrical double layers at the electrode/solution interfaces, it was then possible to calculate, from the total charge passed, the mean oxygen flux through the disc and hence the effective diffusivity, given by Fick's first law as:

$$D = \frac{Qt}{A(c_1 - c_2)} \qquad (1)$$

where D is the effective diffusivity ($cm^2\,sec^{-1}$) Q the oxygen flux ($mol\,sec^{-1}$), t the thickness of the disc (cm), A the area of the disc (cm^2), c_1 the concentration of oxygen in compartment 1 ($mol\,cm^{-3}$), and c_2 the concentration of oxygen in compartment 2 ($mol\,cm^{-3}$). As c_2 was very small ($< 10^{-4}\,c_1$) throughout the experiment it could be ignored for purposes of calculating D. Values of c_1, corresponding to the condition of oxygen saturated $Ca(OH)_2$ solutions at 15, 25 and 35° C, were determined by saturating the solution in both compartments of the cell by bubbling oxygen

TABLE II Solubilities of oxygen in saturated solutions of $Ca(OH)_2$ and water at various temperatures

Temperature (°C)	Oxygen concentration × 10^6(mol cm^{-3})	
	Saturated $Ca(OH)_2$	Water [13]
15	1.49	1.50
25	1.06	1.23
35	0.95	1.03

through them for 72 h and then determining the total oxygen content of the known volume of solution in compartment 2 electrochemically, as for a normal diffusion experiment. Average values of c_1 so obtained were reasonably close to published data for oxygen solubilities in water at the same temperatures [13], as shown in Table II.

3. Results and discussion

3.1. Oxygen diffusivity determinations

Measurements of effective oxygen diffusivity for triplicate specimens of cement paste at the three values of water/cement ratio and temperature investigated are recorded in Table III. The data are also presented in Fig. 3 as best-fit Arrhenius plots, obtained by linear regression analysis. Correlation coefficients for the lines relating to water/cement ratios of 0.4, 0.5 and 0.6 were calculated to be 0.96, 0.96 and 0.95, respectively, and the slopes corresponded to activation energies which are shown with 95% confidence limits in Table IV.

The primary finding is that measured oxygen diffusivities are of similar magnitude to chloride ion diffusivities that were reported previously for hydrated Portland cement pastes. The effect of water/cement ratio on diffusivity is clearly comparable with that observed for chloride and reflects the expected increase in porosity, particularly in the coarser size ranges, as a function of increasing water content [10].

The goodness of fit of the data to straight lines shown in Fig. 3 indicates that, for cement paste of given water/cement ratio, diffusion kinetics were under the control of a single rate-determining step over the temperature range investigated. As the maximum of this temperature range was restricted to 35° C, it is considered unlikely that artefacts of the sort that may have affected a recently reported study of ionic diffusion kinetics in relatively immature (28 day old) cement pastes over the range 20 to 60° C [12] would have been significant. Earlier investigators have shown that temperature-induced alterations in the pore structure of mature hydrated Portland cements start to become noticeable above approximately 50° C [14].

TABLE III Influence of water/cement ratio and temperature on effective diffusivity of oxygen in hardened cement pastes

Water/cement		$D \times 10^8$ (cm^2 sec^{-1})		
		15° C	25° C	35° C
0.4		1.00	1.18	1.62
		0.97	1.48	1.73
		1.02	1.27	1.66
	Average	0.99	1.31	1.67
0.5		1.23	1.61	1.98
		0.99	1.37	2.11
		1.17	1.58	2.04
	Average	1.13	1.52	2.04
0.6		2.01	2.12	2.73
		1.78	2.31	2.86
		1.69	2.16	2.60
	Average	1.83	2.20	2.71

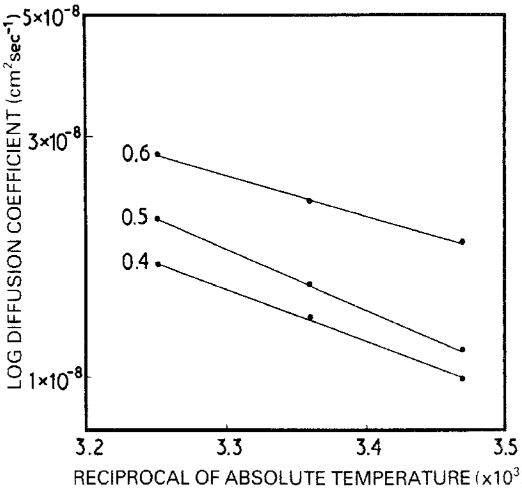

Figure 3 Arrhenius plots of oxygen diffuvisity for pastes of water/cement ratio 0.4, 0.5 and 0.6.

Activation energies for oxygen diffusion in the hardened cement pastes have values which are roughly half those recorded previously for chloride diffusion and exhibit analogous variation with water/cement ratio [10]. Thus the activation energies at water/cement ratios of 0.4 and 0.5 are of similar magnitude but that at water/cement ratio 0.6 is significantly lower. As discussed previously with reference to chloride, this trend is probably explicable in terms of the effect of water/cement ratio on the continuity of pores within the coarsest size-range present in the materials, as these constitute the least constricted paths for molecular and ionic diffusion [10]. According to the classic model of Powers *et al.* [15, 16], Portland cement pastes of water/cement ratio 0.6 would be expected to contain a residue of unblocked "capillary pores" after hydration for 60 days whilst, at similar maturity, the capillary pores within pastes of water/cement ratios 0.5 and 0.4 would all have become discontinuous as a result of deposition of calcium silicate hydrate gel. The latter is considered to be the major barrier to diffusion since hydrated pastes of the mineral alite (substituted $3CaO \cdot SiO_2$) exhibit activation energies for ionic diffusion similar to those found in Portland cement pastes [17].

TABLE IV Activation energies for oxygen diffusion in hardened cement pastes of various water/cement ratios and comparative data for chloride diffusion

Water/cement	Activation energy (kJ mol^{-1})	
	Oxygen	Chloride [10]
0.4	19.0 ± 0.5	41.8 ± 4.0
0.5	22.0 ± 2.4	44.6 ± 4.3
0.6	14.9 ± 2.8	32.0 ± 2.4

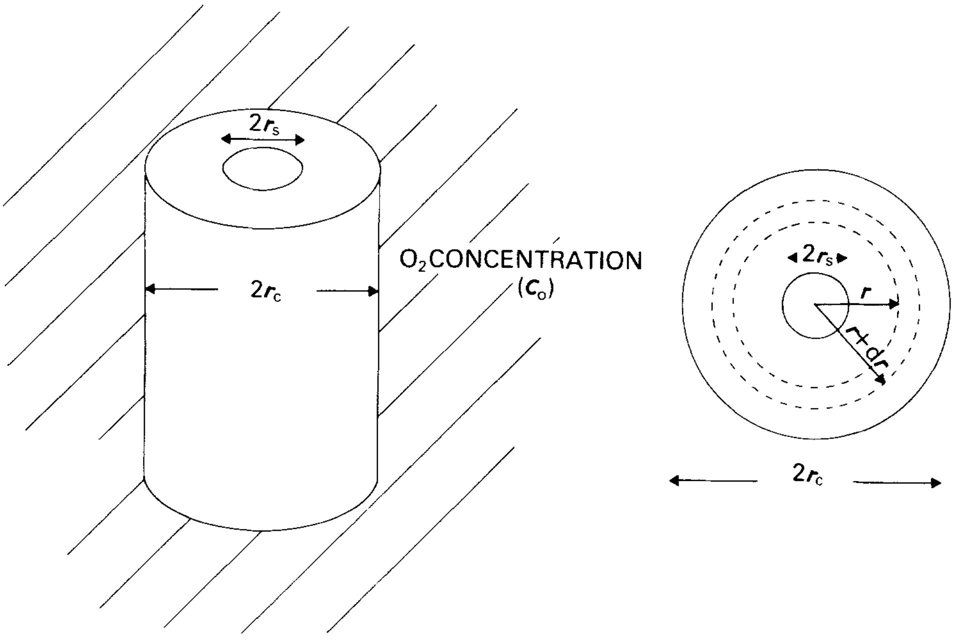

Figure 4 Diffusional model of steel in a cement matrix surrounded by an aqueous oxygen-containing medium.

Estimation and analysis of the pre-exponential components of the diffusion coefficients would have been of interest as these are made up of several terms, dependent on the effective porosity, path tortuosity and entropy of activation [18]. This was not considered feasible, however, since insufficient data were available to allow reasonable accuracy in making the necessary extrapolation of the Arrhenius plots to the zero axis of reciprocal temperature.

3.2. Implications for electrochemistry of embedded steel

In the light of the foregoing results, it is of interest to examine the critical conditions for the transition in behaviour of embedded steel from passivity to cathodically restrained general dissolution for a simple model system.

Consider the arrangement illustrated in Fig. 4, in which a steel bar of radius, r_s, is embedded along the axis of a cylindrical matrix of hydrated cement of radius, r_c, surrounded by an aqueous medium of oxygen concentration, c_o. Assuming oxygen is supplied to the steel only by radial diffusion through the matrix and is cathodically reduced instantly on arrival at the steel surface, the steady-state flux of oxygen, J, through an element situated at a distance, r, from the axis and of unit length parallel to the axis will be constant and given by:

$$J = 2D\pi r \frac{\mathrm{d}c}{\mathrm{d}r}\ \mathrm{mol\,sec^{-1}} \tag{2}$$

Integration between the limits r_c and r_s gives:

$$J = 2D\pi c_o[\ln(r_c/r_s)]^{-1}\ \mathrm{mol\,sec^{-1}} \tag{3}$$

The limiting cathodic current density for reduction of oxygen, i_{lim}, is thus:

$$\begin{aligned} i_{\mathrm{lim}} &= 2FJ(\pi r_s)^{-1} \\ &= 4FDc_o[r_s \ln(r_c/r_s)]^{-1}\ \mathrm{A\,cm^{-2}} \end{aligned} \tag{4}$$

where F is Faraday's number (96 500 C/g eq.).

The condition for a transition from passivity to cathodically restrained general dissolution is:

$$i_p > i_{\mathrm{lim}} \tag{5}$$

where i_p represents the anodic leakage current density of the passive steel surface. Hence

$$i_p > 4FDc_o[r_s \ln(r_c/r_s)]^{-1} \tag{6}$$

or, since $r_c > r_s$

$$r_c > r_s \exp[4FDc_o(i_p r_s)^{-1}] \tag{7}$$

Thus the critical depth of cover, $r_c - r_s$, at which the transition occurs is given by:

$$r_c - r_s > r_s\{\exp[4FDc_o(i_p r_s)^{-1}] - 1\} \tag{8}$$

The above relationship has been plotted in Fig. 5 to show limits of matrix cover depth and steel bar radius corresponding to the boundary between the two electrochemical states for the following assumed values: D ($2.2 \times 10^{-8}\ \mathrm{cm^2\,sec^{-1}}$), c_o ($10^{-6}\ \mathrm{mol\,cm^{-3}}$) and i_p ($2 \times 10^{-8}\ \mathrm{A\,cm^{-2}}$).

From this simple analysis, it therefore appears that the transition from passivity to cathodically restrained

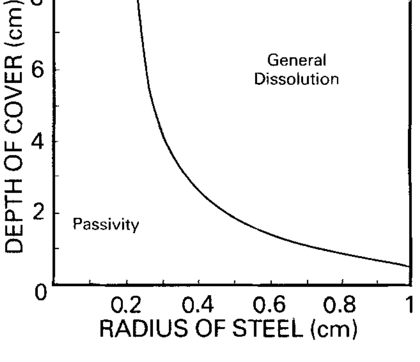

Figure 5 Predicted relationship between cover depth, steel radius and electrochemical condition.

general dissolution may be expected to occur at realistic values of cover depth and bar radius even in well oxygenated waters.

4. Conclusion

The electrochemical technique devised for study of oxygen diffusion kinetics in water-saturated hardened cement pastes yields diffusivity values of similar magnitude to previously measured diffusivities of chloride ion in these materials. The observed dependence of oxygen diffusion rates on water/cement ratio also accords with expectations. It is therefore considered that the method is basically sound and that, with minor adaptations, it may be useful for investigation of oxygen diffusion kinetics in concretes and other cement-based materials.

Activation energies for the diffusion of oxygen in hardened Portland cement pastes were found to be smaller than those reported previously for ionic diffusion but to show a similar pattern of variation as a function of water/cement ratio. The activation energy recorded for mature hydrated paste of water/cement ratio 0.6 was significantly lower than those for specimens of water/cement ratios 0.5 or less; this observation is believed to reflect the presence of residual unconstricted capillary porosity in the former material only.

By analysis of a simple diffusional model, it has been shown that the electrochemical state of steel bars, embedded in water-saturated cement matrices of comparable oxygen diffusivity to those used in the present investigations, may be expected to change from passivity to cathodically restrained general dissolution at realistic ratios of cover thickness to bar radius. Further consideration will be given to the applicability of this prediction under less idealized conditions in a forthcoming paper on the corrosion behaviour of steel in saturated concretes [19].

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