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DIFFUSION IN CEMENTITIOUS MATERIALS:
II. FURTHER INVESTIGATIONS OF CHLORIDE AND OXYGEN DIFFUSION IN WELL-CURED OPC AND OPC/30%PFA PASTES

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ABSTRACT

Steady-state diffusion of dissolved oxygen and chloride ions in hydrated OPC and OPC/30%PFA pastes, hydrated for 2 weeks at 20°C and 10 weeks at 38°C, was studied at water/binder (w/s) ratios 0.4, 0.5, 0.6 and 0.7. Total porosity and a simple measure of capillary porosity, the volume fractions of the water lost in specimens from a saturated surface dry condition to a near-constant weight at 90.7% relative humidity, were also determined. The diffusion rate of chloride ions diminished markedly, to very low values, as the capillary porosity approached zero. For a given w/s ratio or capillary porosity the chloride ion diffusion coefficient for OPC/30%PFA pastes was about one order of magnitude smaller than that for OPC pastes. The rate of diffusion of dissolved oxygen also diminished as the capillary porosity reduced but it was still significant as the capillary porosity approached zero. For a given capillary porosity the oxygen diffusion coefficient for OPC/30%PFA pastes was about 30% smaller than that for OPC pastes. The results support the view that chloride ion diffusion in pastes of low capillary porosity is retarded by the surface charge of the hydrated cement gel. In contrast, the hydrated cement gel is much more permeable to the similarly-sized, neutral oxygen molecule.

Introduction

Steady state ionic diffusion in hydrated cement pastes has been studied extensively[1-9]. It has been generally found[1-3] that the w/s ratio has a marked effect on ionic diffusion. This has been attributed to the influence of the variation of the pore structure with w/s ratio. Although PFA blended cement paste has been shown by mercury intrusion porosimetry to have a greater total porosity and apparently coarser pore structure in comparison with OPC paste of similar w/s ratio, it offers a much greater resistance to ionic diffusion[1,2,4]. However, the coarser pore structure found for the PFA blended paste has been considered[10] as an artefact due to the disruption of the relatively large but discontinuous, thin-walled pores at high pressure during the mercury intrusion.

Hydrated cement pastes of low w/s have been shown[5,6] to provide much greater resistance to the diffusion of cations than anions. This is in contrast to diffusion in bulk aqueous solutions where similar diffusion coefficients for sodium and chloride ions are found. The activation energies for chloride diffusion in hydrated OPC and C_3S pastes are reported[1-3,5] to be much higher than those in bulk solution. This prompted Page et al[1,2] to suggest that the rate-limiting process controlling chloride diffusion in OPC pastes was associated with some form of surface interaction although no clear picture of these interactions was given. Goto and Roy[5] concluded that the electrical double layer developed at the interface between the pore solution and the cement matrix can influence ionic diffusion, but the thickness of the double layer that they assumed appears excessive in comparison with the value calculated by Yu and Page[7].

It is therefore important to devise experiments to evaluate the extent to which ionic diffusion is affected by the surface charges of cement hydrates before attempting to formulate mechanisms through which the rate of ionic diffusion is determined. An approach which has been developed at Aston University[7], involves comparative study of chloride and dissolved oxygen diffusion in hydrated cement pastes. The two species have similar diffusion coefficients in infinitely dilute solutions, 2.1×10^{-5} and $2.03\times10^{-5}cm^2/s$ at 25°C respectively[11]. Oxygen, however, being a neutral molecule without dipolar character, is not expected to encounter electrostatic surface interactions of the kind that may influence the transport of chloride ions in hydrated cement pastes. The difference in the rates of diffusion for the two species can thus be considered to reflect the extent to which ionic diffusion is affected by the surface charges of the cement hydrates.

A previous investigation carried out by the authors[7] has shown that chloride ions are retarded more than oxygen molecules when diffusing through dense OPC and OPC/20%PFA pastes, suggesting a large effect of the surface charge on chloride diffusion. The aim of this project was to extend the previous work by measurement of oxygen and chloride diffusion kinetics in a wider range of well-cured saturated cement pastes. To aid the interpretation of the diffusion results, total porosity and the volume fraction of the water lost in specimens from a saturated surface dry condition to a near-constant weight at 90.7% relative humidity were also determined.

Experimental

Materials and Sample Preparation

The compositions of the OPC and PFA used, expressed in percentages by weight of the constituent oxides, are shown in Table 1. Blended cements were obtained from a mixture of OPC and 30%PFA.

OPC and OPC/30%PFA pastes were obtained by hand mixing with deionised water for about 5 minutes to produce mixtures of w/s ratios of 0.4, 0.5, 0.6 and 0.7. The mixes were poured into

TABLE 1
Chemical Analysis of OPC and PFA (%).

oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	LOI
OPC	63.58	21.20	5.34	2.62	3.38	1.30	0.09	0.75	1.53
PFA	1.45	48.20	32.20	8.02	0.52	0.66	0.98	2.85	3.84

cylindrical PVC containers, 49mm in diameter by 75mm in height, and compacted by means of vibration. The cylinders were sealed and rotated end over end at a speed of 8rpm for at least 24 hours in order to minimise sedimentation of the cement particles. After curing at 22°C for 2 weeks, the cylinders were demoulded, immersed in 35mM NaOH solution and stored in a curing room at a temperature of 38±2°C for 10 weeks to accelerate cement hydration and pozzolanic reaction of the PFA.

Thin discs (approximately 3mm thick) were cut from the central regions of each cylinder by means of a diamond saw, lubricated with deionised water. The surfaces of the discs were ground with grade 600 emery paper and rinsed with deionised water, before being fitted into the appropriate diffusion cells. For every w/s ratio and binder being investigated, 4 or 5 replicate cells were set up and placed in a waterbath, which was maintained at a constant temperature of 25°C.

Oxygen diffusion

The oxygen diffusion cell used was similar to that described by Yu and Page[7]. The cell consisted of two compartments containing an anode and a cathode respectively. The cathode compartment was initially filled with a deaerated solution of 35mM NaOH, whilst oxygen gas was bubbled through the anode compartment which also contained 35mM NaOH solution. The diffusion of oxygen was determined electrochemically by the consumption of diffused oxygen repeatedly over a time interval of 2 or 3 days until more than 5 near-constant values of the flux were obtained. The effective diffusion coefficients of oxygen (D_o) were calculated from Fick's first law and Faraday's law as described in the previous paper[7].

Chloride diffusion

Chloride diffusion experiments were carried out in parallel to oxygen diffusion experiments for a set of accompanying specimens. This was achieved by use of the ionic diffusion cell described by Page et al[1]. At the start of the experiment, the high concentration side of the cell was filled with a solution containing 1M NaCl in 35mM NaOH while the low concentration side was filled with 35mM NaOH solution. The chloride concentration on the low concentration side was determined by means of a standard spectrophotometric technique[12]. The calculation of the chloride diffusion coefficient (D_{cl}) was the same as that described in a previous publication[1].

Porosity

After the oxygen diffusion experiments, the water-saturated discs were removed from their cells and used for bulk density and porosity measurement. The specimens were dried at 90.7% relative humidity by placing them above a saturated salt solution of barium chloride contained in a desiccator until a near-constant sample weight was obtained. The weight loss on drying was then converted to volume fraction of the bulk paste. This particular measure of coarse capillary porosity corresponds to pores wider than about 30nm[13] and was used because:
(i) it avoided unrealistic drying, which can produce porosity artefacts[14].
(ii) it was found to correlate with another transport property, rate of water absorption[13].
The specimens were finally dried at 105°C and the total porosity values calculated.

Results and Discussion

The experimentally obtained diffusion coefficients, total porosities and the volume fractions of the water lost on drying at 90.7% relative humidity are shown in Tables 2 and 3 for the OPC and OPC/30%PFA pastes respectively. These values show very close consistency between the replicate samples.

TABLE 2
Experimental results obtained for hydrated OPC pastes

W/C	D_o ($\times 10^{-8} cm^2/s$)	D_{cl} ($\times 10^{-8} cm^2/s$)	Capillary Porosity (%)	Total Porosity (%)
0.4	9.78	4.35	4.33	40.18
	10.00	3.75	4.32	40.40
	8.49	3.99	4.05	40.43
	9.00	4.01	4.56	40.56
	9.40	3.65	4.32	40.59
Average	9.33	3.95	4.32	40.41
0.5	9.63	7.16	8.34	47.16
	10.41	7.93	8.34	47.02
	10.87	8.06	8.30	47.19
	10.68	8.06	8.48	47.01
Average	10.40	7.80	8.36	47.10
0.6	14.24	12.99	16.34	52.20
	11.37	13.81	17.84	50.97
	12.67	12.45	16.06	50.89
	16.65	10.40	16.61	52.17
	13.29	13.37	19.03	51.57
Average	13.64	12.60	17.18	51.56
0.7	19.08	19.65	24.29	55.26
	17.37	19.86	24.51	54.95
	24.47	22.16	25.18	55.51
	20.99	21.28	24.15	55.18
	26.84	24.35	26.19	56.25
Average	21.75	21.46	24.86	55.43

Figure 1 demonstrates that, although the total porosities of OPC/30%PFA pastes are slightly greater than those of OPC pastes of the same w/s ratio, the reverse is true for capillary porosities. This is a reflection of the greater gel porosity due to the production of additional calcium silicate hydrate (CSH) gel associated with the pozzolanic reaction of PFA. However, Figure 1 does not give any indication of the connectivity or tortuosity of the capillary pores, which are thought to play a vital role in the transport properties of the different pastes.

The average values of diffusion coefficients of chloride ions and oxygen are plotted in Figure 2

TABLE 3
Experimental results obtained for hydrated OPC/30%PFA pastes

W/C	**D_o (x10^{-8}cm^2/s)**	**D_{cl} (x10^{-8}cm^2/s)**	**Capillary Porosity (%)**	**Total Porosity (%)**
0.4	6.33	0.33	3.11	43.37
	5.54	0.52	3.10	43.29
	6.24	0.33	2.96	43.20
	5.56	0.39	3.11	43.22
	5.36		3.07	43.25
Average	5.79	0.39	3.07	43.27
0.5	7.00	0.35	5.15	48.84
	6.62	0.57	5.25	48.30
	6.41	0.42	4.95	48.36
	6.63	0.43	5.88	49.26
		0.39		
Average	6.67	0.43	5.31	48.69
0.6	8.80	1.04	8.83	54.28
	6.94	0.82	9.28	54.58
	7.58	0.72	9.68	54.73
	6.72	1.01	8.74	54.53
		0.93		
Average	7.51	0.90	9.13	54.53
0.7	9.25	0.89	13.92	58.29
	9.30	1.06	13.06	58.26
	8.63	1.10	13.68	58.46
	8.35	1.14	13.75	58.22
		0.96		
Average	8.88	1.03	13.60	58.31

against the w/s ratio. Compared with the OPC paste of the same w/s ratio, the OPC/30%PFA paste provides greater resistance to the diffusion of both species, as reported in the literature[1,2,7]. Oxygen is also shown to have a greater diffusion coefficient than chloride ion for each paste, which is in agreement with the results obtained in the previous investigation[7]. For the OPC paste, the difference between the oxygen and chloride diffusion coefficients is very large at lower w/s ratio but becomes almost zero when the w/s is 0.7, whilst for the OPC/30%PFA pastes, this difference is very large at all the w/s ratios investigated.

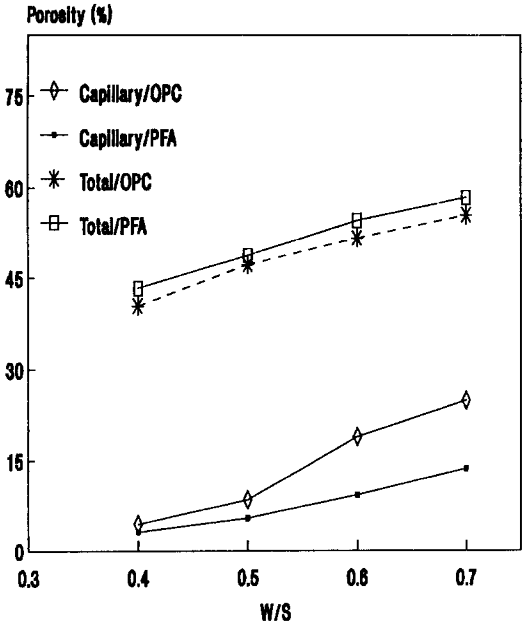

FIG. 1
Capillary and total porosities of pastes versus w/s ratio

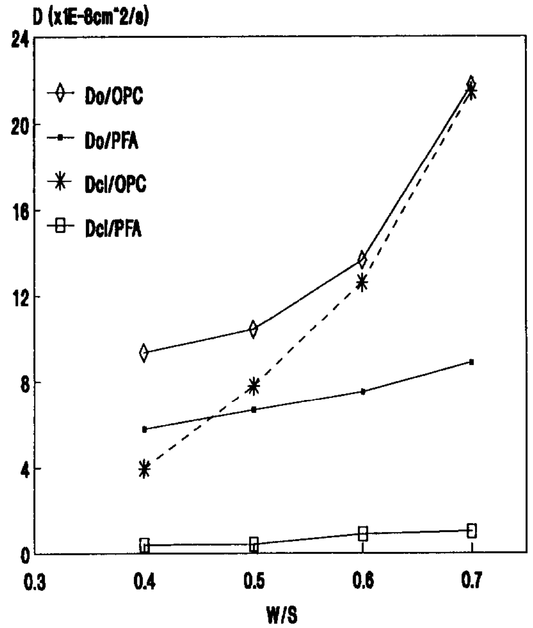

FIG. 2
Diffusion coefficients for oxygen and chloride ion versus w/s ratio

Chloride and oxygen diffusion coefficients are shown in Figure 3 to diminish as the capillary porosity diminishes for both OPC and OPC/30%PFA pastes. Chloride diffusion coefficients for both cement systems tend to zero as the capillary porosities approach zero. This implies that the cement hydrates have a low permeability to chloride ions. The diffusion coefficients for the OPC/30%PFA pastes are markedly smaller than those of OPC pastes for the same capillary porosity. This suggests that there is a greater continuity of the capillary pore system in the OPC pastes. On the other hand, oxygen diffusion coefficients do not tend to zero as the capillary porosity approaches zero. This indicates that the cement hydrates are permeable to oxygen. Furthermore, the results suggest that the OPC hydrates are slightly more permeable to oxygen than those of OPC/30%PFA. This may be associated with the smaller proportion of $Ca(OH)_2$ in the OPC/30%PFA pastes since $Ca(OH)_2$ is coarsely crystalline in comparison with CSH.

The sizes of the oxygen molecule and the chloride ion are similar and their diffusion coefficients in bulk aqueous solutions are comparable. Thus the two species might be expected to diffuse at similar rates in very porous, hydrated cement pastes. The large differences between oxygen and chloride diffusion coefficients observed for all the OPC/30%PFA and the OPC pastes of low capillary porosity suggest that chloride diffusion kinetics in these pastes are greatly restricted by the interactions between the migrating chloride ion and the electrostatically charged pore walls or by the electrical double layer at the interface between the pore walls and pore solution.

The ratio of oxygen to chloride diffusion coefficients (D_o/D_{cl}) may be considered as a numerical measure of the effect of the surface charge on chloride diffusion. Figure 4 shows the variation of this ratio with D_{cl}, together with data obtained from the earlier study[7] for OPC and OPC/20%PFA pastes at w/s ratios 0.35, 0.5 and 0.6. It may be seen from this figure that as the pastes become less permeable, they provide progressively more resistance to the diffusion of

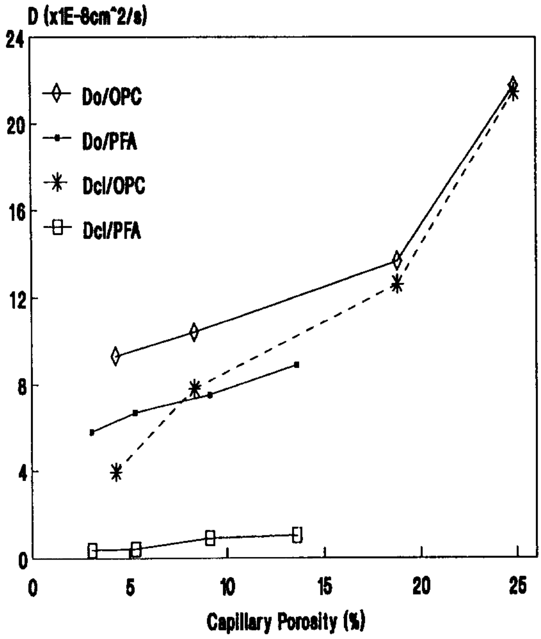

FIG. 3
Diffusion coefficients for oxygen and chloride ion versus capillary porosity

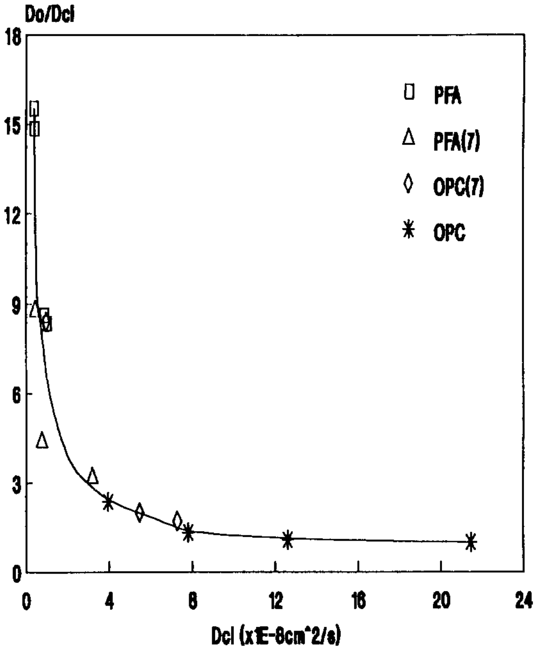

FIG. 4
Ratio of oxygen to chloride diffusion coefficient

chloride ion than to the diffusion of the neutral oxygen molecule.

The ratio (D_o/D_{cl}) can be as great as about 15 at very small values of the chloride diffusion coefficient. This suggests that the diffusion rates of chloride ions in the pastes of low permeability are predominantly determined by the effect of surface charge rather than purely geometrical restrictions.

Conclusions

This study has shown that the diffusion rate of chloride ions through mature, saturated cement pastes diminished markedly with a reduction of w/s ratio and tended to a very low value as the capillary porosity approached zero. For a given w/s ratio or a given capillary porosity the chloride diffusion coefficients for OPC/30%PFA paste were about one order of magnitude smaller than those for OPC pastes. The diffusion of dissolved oxygen also diminished with a reduction of w/s ratio but did not tend to very low values as the capillary porosity approached zero. For a given w/s ratio or a given capillary porosity the oxygen diffusion coefficients for OPC/30%PFA pastes were about 25% smaller than those for OPC pastes. The ratio of the diffusion coefficients for oxygen to chloride ion increased from values close to one, in permeable pastes, up to values of around 15 in low-permeability, OPC/30%PFA pastes. This supports the view that diffusion of chloride ions is retarded by the surface charge of the hydrated cement gel in pastes with a low capillary porosity. In contrast, the hydrated cement gel is much more permeable to the similarly sized, neutral oxygen molecule.

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