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Oxygen diffusion through hydrophobic cement-based materials

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ABSTRACT

The oxygen diffusion coefficient through hydrophobic cement-based materials fully immersed in water was determined by potentiostatic measurements on concrete and by the use of a diffusion cell on cement pastes and mortars. The obtained results show that very high oxygen diffusion occurs through cement paste, mortar and concrete made with hydrophobic admixture as opposed to negligible diffusion through the reference cement matrix without admixture. Moreover, the oxygen diffusion coefficients measured through hydrophobic cement matrices immersed in water were comparable with those reported in literature for unsaturated cement materials in air. These experimental results appear to confirm that oxygen dissolved in water directly diffuses as a gaseous phase through the empty pores of a hydrophobic cement matrix. This could explain the severe corrosion of steel reinforcement embedded in cracked hydrophobic concrete immersed in an aqueous chloride solution observed in a previous work.

1. Introduction

The protection provided by concrete to reinforcing bars may be reduced and even cancelled by high concrete porosity or the presence of cracks. In both cases, there is rapid penetration of chloride ions, which can destroy the passive oxide film protecting the rebars from corrosion, or carbon dioxide which neutralizes the alkalinity of the aqueous solution in the concrete pores assuring the stability of the passive oxide film [1].

However, steel corrosion would not occur if water, which acts as a carrier for the diffusion of chloride ions and is the medium where corrosion reactions develop, is permanently prevented from wetting the porous structure of the concrete.

The water in contact with a porous hydrophilic material, such as concrete, penetrates the material by means of capillary forces following the Washburn equation, $p=(2\gamma/r_c)\cos\sigma$, where p is the capillary pressure, γ represents the liquid surface tension, r_c is the capillary pore radius, and σ is the contact angle. A water droplet, on a hydrophilic solid, wets the solid surface by spreading itself and by absorption through the solid porosity. The contact angle becomes less than 90°, p becomes positive and the liquid fills the pore spontaneously. However, the molecular attraction between water and the concrete pore walls can be lowered by surface treatment using impregnation with hydrophobic agents, such as those based on alkyl–alkoxy–silane [2–18]. In this case, the contact angle becomes higher than 90°, the water droplet keeps itself spherical, and an external pressure p (in this case negative) is necessary to allow the liquid to penetrate the solid porosity. Their alkoxylic groups are chemically bound to the hydrated silicates in the concrete by a condensation reaction, while their hydrophobic alkylic groups come out on the pores surface [19]. Hydrophobic treatments, differ from waterproofing ones, only covering the pore walls by leaving pores practically empty. Capillary pore size in concrete mainly varies from 100 Å to 10,000 Å. Acrylic agents and epoxy resins, due to their large molecular size, can only film the surface by waterproofing it. On the contrary, silanes can penetrate concrete since their molecular size varies from 10 Å to 20 Å [7].

Hydrophobic treatments hinder liquid water to penetrate the structure when pressure is not excessively high. However, differently from waterproofing treatments, they allow water vapour permeation, and in general gas permeation, leading to water leakage from the structure.

The effectiveness of mortar surface treatments with alkyl–alkoxy–silane against water penetration has been demonstrated [15,19,20]. But, their efficiency with time depends on the alkali resistance of the applied compounds, their penetration depth, their resistance to atmospheric agents, and the integrity of the structure [20–24]. Therefore, hydrophobic agents have been recently added in the concrete mixture directly in order to make both the surface and the whole concrete bulk hydrophobic [25–30]. In this way, bulk hydrophobization could cancel the detrimental effect of concrete cover cracking as the possible fracture surfaces coming from concrete cover cracking would be hydrophobized.

The results obtained showed that in the absence of cracks, the hydrophobic concrete, fully immersed in a chloride aqueous solution, very effectively protects steel reinforcement against corrosion. On the other hand, in the presence of cracks, more than ten-fold higher corrosion currents were monitored with respect to those in the reference concrete specimens without the hydrophobic admixture [31].

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Table 1
Concrete mixture proportions.

Ingredients	Amounts (kg/m^3)			
	$w/c=0.45$	$w/c=0.45$ hydrophobic	$w/c=0.80$	$w/c=0.80$ hydrophobic
Portland cement	350	350	260	260
Water	158	149	208	202
Sand	775	775	830	830
Coarse aggregate	1160	1160	1090	1090
Superplasticizer	3.5	3.5	–	–
Hydrophobic admixture	–	15.6	–	11.6

The proposed hypothesis to explain these unexpected results admits that oxygen diffusion, feeding the corrosion process, could directly occur in a gaseous phase through the unsaturated porosity of the immersed hydrophobic concrete, while in concrete without silane, oxygen diffuses much slower through the water filling the pores of the saturated concrete [31].

2. Scope

The aim of the present paper is to confirm the validity of the above mentioned hypothesis. With this in mind, the oxygen diffusion coefficient of hydrophobic paste, mortar and concrete with different water–cement ratio was measured when fully immersed in water.

The oxygen diffusion through concrete was studied by means of electrochemical potentiostatic measurements on a steel plate embedded in the concrete specimen. The steel plate was polarized at a constant potential and the resultant oxygen reduction current flow was detected.

For cement pastes and mortars, a diffusion cell was manufactured instead, where the specimens acted as diaphragms between two water compartments with different oxygen concentrations. In this latter case, the cement specimens were either bulk or surface hydrophobic, in order to obtain further confirmation of the above mentioned hypothesis, as a similar behavior was expected in the two different cases.

3. Experimental

3.1. Materials

Commercial portland cement type CEM II/B-M 32.5, crushed aggregate (25 mm maximum size) and natural sand (2 mm maximum size) were used.

A 40% aqueous solution of naphtalene-based admixture was used to make the concrete with $w/c=0.45$ as flowable as the concrete with $w/c=0.80$.

A 45% aqueous emulsion of butyl–ethoxy–silane was used to manufacture bulk hydrophobic cement paste, mortar and concrete. A commercial product based on siloxanic resins was used to make the cement paste and mortar surface hydrophobic.

Bare steel plates were embedded in the concrete specimens to act as electrodes to be polarized, in order to carry out electrochemical measurements.

3.2. Mixture proportions

Concrete with $w/c=0.45$ and $w/c=0.80$ with and without hydrophobic admixture was used to manufacture the specimens. The amounts of concrete ingredients reported in Table 1 were mixed.

Cement mortars with $w/c=0.5–0.6–0.7$ were manufactured by adding the hydrophobic admixture. Natural sand (2 mm maximum size) was used with an aggregate to cement ratio equal to 3.

Cement pastes with $w/c=0.4–0.5–0.6–0.7$ were manufactured by adding the hydrophobic admixture. As reference, a cement paste without this admixture was manufactured with $w/c=0.6$.

Bulk hydrophobic cement materials were manufactured by adding 2% of the active ingredient by mass of cement in the mixture.

The high w/c sometimes adopted combined with the low strength type of cement used are justified by the following reasons:

- the hydrophobic action caused by the admixture addition is much less effective when the cement matrix porosity is lower [24],
- the necessity to obtain an open porosity as wide as possible, in relation to the curing achieved at the time of the measurement [32].

3.3. Specimens

3.3.1. Concrete specimens

A prismatic specimen (100 × 100 × 400 mm) was manufactured for each w/c adopted (0.45 and 0.80) with and without the hydrophobic admixture. The silane addition to the concrete mixture caused a compressive strength loss of about 10–20%, recorded at 1–7–28 days of curing time with respect to concrete without silane, in agreement with data reported in literature [25,31].

In each concrete specimen, a single steel plate (70 × 1 × 360 mm) was embedded with a 30 mm cover (Fig. 1). The electrical connections required by the electrochemical measurements were carried out as described in previous works [31].

All the specimens were kept for 48 h at 100% R.H. and, after demoulding, they were air dried for 1 month at room temperature. In order to make the oxygen flow unidirectional and perpendicularly directed to the steel plate through the concrete cover, all the specimen sides not intended to be involved in the oxygen diffusion process were epoxy coated.

3.3.2. Cement mortar and paste specimens

Cement mortar and paste were cast in short truncated PVC pipes in order to obtain flat cylindrical specimens with 50 mm diameter and 5–15 mm thickness. After 1 day of wet curing and another day of air curing, the specimens were dried to constant weight in a drying oven at 60 °C.

At this time, half of the specimens, prepared without hydrophobic admixture addition, were made surface hydrophobic by applying a commercial siloxane-based product. The penetration depth of this surface treatment was equal to about 2 mm.

Once the cement mortar and paste specimens were checked by microscopic observation to make sure that no micro-cracking occurred, the lateral surface of these cylindrical specimens was epoxy coated in order to allow oxygen diffusion along the direction perpendicular to the cylinder bases only. All the specimens were then stored in a drying chamber before undergoing the diffusion test.

3.4. Testing of specimens

3.4.1. Concrete specimens

The effective [33] oxygen diffusion coefficient through concrete was calculated electrochemically by measuring the oxygen reduction

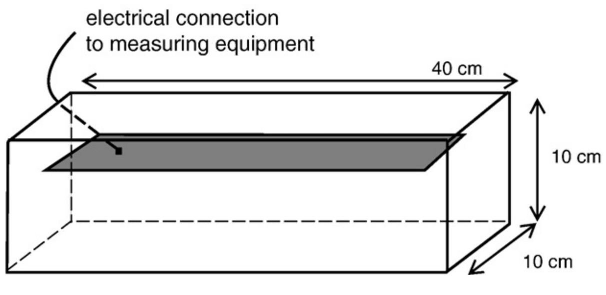

Fig. 1. Prismatic reinforced concrete specimen.

current under a steady potential, avoiding both oxygen accumulation on the cathode and water reduction.

After about 2 months of full immersion in water, the steel plates embedded in the concrete specimens were cathodically polarized at $E = -950$ mV SCE (with respect to a reference Saturated Calomel Electrode) by means of a potentiostat and the resulting current was monitored until a steady state was reached. The reference saturated calomel electrode as well as the graphite counterelectrode required for measurement of the current were immersed under water. The establishment of steady state boundary conditions was checked by increasing slightly the polarization potential and verifying that there was no current increase. When this occurs, all oxygen reaching the steel plate is consumed in the cathodic reaction, thus the rate of oxygen diffusion is identical to its consumption rate at the cathode, since hydrogen evolution due to water reduction is negligible at this potential [34].

In these conditions, by combining Faraday's law with Fick's first law, the diffusion coefficient D is given by:

$$D = il / nFS(c - c_0)$$

where i is the steady cathodic current (μA), l is the concrete cover thickness (30 mm) on the steel plate, $n = 4$ are the exchanged electrons for each oxygen molecule, F is Faraday's constant, S is the steel plate area (252 cm^2), c is the oxygen concentration in water (7 ppm), $c_0 = 0$ is the oxygen concentration on the steel plate.

3.4.2. Cement mortar and paste specimens

In this case, the oxygen diffusion coefficient was measured by means of a diffusion cell. The cell was made of plexiglass with two compartments (A, the measuring one, and B, the feeding one, as shown in Fig. 2) separated by the cement mortar or paste specimen, acting as a flanged diaphragm sealed by means of flat rubber rings.

The diffusion cell, with the compartments filled up with water, was introduced into a thermostatic bath at 25 °C in order to avoid thermal changes which could influence the diffusion coefficient value as well as the oxygen solubility in water in the feeding compartment (B in Fig. 2). The oxygen flow through the specimen was continuously monitored by means of a digital oxymeter (AMEL Mod.332 with a ±0.001 ppm resolution) placed in the measuring compartment A, where a magnetic stirrer was present to make oxygen dissolution easier, thus preventing the diffusive motion of oxygen in water.

The two compartments of the diffusion cell were then first deaerated by means of a constant flow of nitrogen. After 4 h, this flow was stopped in the measuring compartment A and monitoring of the oxygen amount in this compartment was started. In this way, the oxygen trapped in the porous cement matrix of the specimen was driven out until steady state conditions were reached. This was assumed as base line for the measurements.

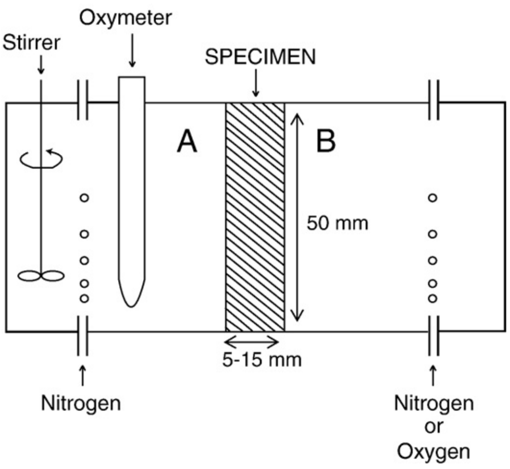

Fig. 2. Diffusion cell for cement paste and mortar.

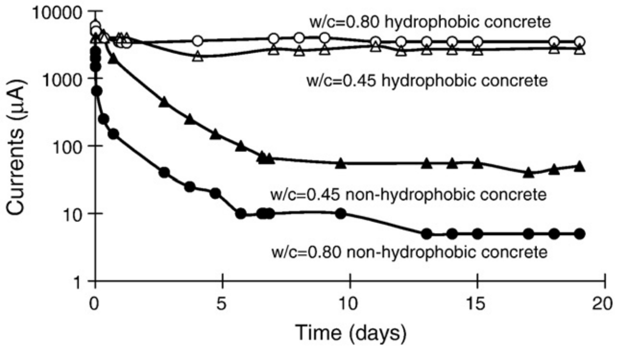

Fig. 3. Polarization currents as a function of time at $E = -950$ mV SCE for the steel plates embedded in the concrete specimens with and without hydrophobic admixture.

At this stage, the constant flow of nitrogen in the feeding compartment B was replaced with oxygen in order to obtain a concentration gradient between the opposite faces of the specimen which induces the oxygen diffusion process. As a consequence, a linear increase in oxygen concentration with time was detected by the oxymeter. The slope of this linear trend was related to the oxygen diffusion coefficient by Fick's first law. Indeed, only a pseudo-steady state could be established in this way, due to the negligible concentration change produced by the diffusion process with respect to the oxygen initial concentration in the measuring compartment A [35]. This assured a constant flow through the specimen, as also confirmed by the linear trend.

Finally, the oxygen diffusion coefficient, assumed to be independent of concentration, was calculated by

$$D = \Delta N l / S(c - c_0)\Delta t$$

where ΔN represents the moles of oxygen passed during the time Δt through the surface S (633 mm^2) of the specimen, whose thickness is l (5–15 mm), and c, equal to 1.23×10^{-3} mol/l, is the oxygen solubility in water at 25 °C [22], while c_0 indicates the oxygen initial concentration in the measuring compartment represented by the base line.

Concerning with hydrophobic cement pastes, diffusion measurements were carried out also at $T = 15$ °C and $T = 35$ °C in order to calculate the activation energy of oxygen diffusion through bulk hydrophobic cementitious matrices by means of the logarithmic form of the Arrhenius equation. The values of oxygen solubility in water at different temperatures were taken from the literature [36].

4. Results and discussion

4.1. Concrete specimens

Fig. 3 shows the oxygen reduction currents obtained by the steel plate polarization at −950 mV SCE as a function of time for hydrophobic or non-hydrophobic concrete with two different *w/c*.

The very high current values initially measured for all the specimens, are due to the oxygen content in the air trapped in the concrete after casting. However, when the specimens are immersed in

Table 2
Oxygen diffusion coefficients for concrete specimens with and without hydrophobic admixture.

w/c	D (cm^2/s)	
	Hydrophobic concrete	Non-hydrophobic concrete
0.45	3.6×10^{-4}	7.7×10^{-6}
0.80	5.0×10^{-4}	7.0×10^{-7}

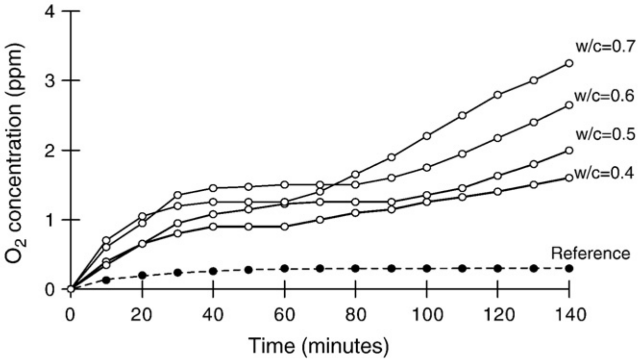

Fig. 4. Concentration of the oxygen diffused through bulk hydrophobic cement pastes with different *w/c* as a function of the diffusion time.

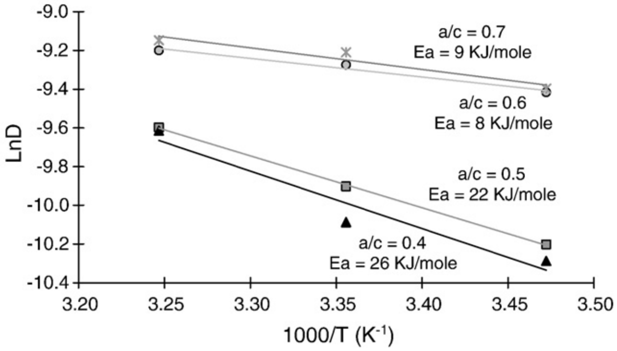

Fig. 5. Activation energies for oxygen diffusion process through full-immersed hydrophobic cementitious matrices.

water, these very high current values drop rapidly down to very low values in non-hydrophobic concrete, due to water saturation of the concrete which slows down the oxygen diffusion and its availability for the cathodic reaction on the steel plate. On the contrary, in hydrophobic concrete, water saturation is hindered and consequently large amounts of oxygen can be continuously supplied on the steel plate to be reduced.

In Table 2 the oxygen diffusion coefficients are reported as calculated by the experimental results for hydrophobic or non-hydrophobic concrete with two different *w/c*.

The values obtained for non-hydrophobic concrete are in good agreement with the values reported in the literature for water-immersed concrete [37]. On the other hand, hydrophobic concrete, even when immersed in water, shows much higher oxygen diffusion coefficients which are surprisingly similar to those reported in the literature for unsaturated concrete in air [38,39].

4.2. Cement mortar and paste specimens

Fig. 4 shows, as an example, the curves drawn from experimental data from which the oxygen diffusion coefficient through bulk hydrophobic cement pastes with different *w/c* was obtained. The reference curve was obtained by using a methyl-methacrylate specimen (4 mm thick), through which the oxygen diffusion could be neglected.

The diffusion coefficients calculated from the slope of the linear trend of the curves related to oxygen diffusion through the cement mortar or paste specimens fully immersed in water (Fig. 4), are reported in Table 3 for either bulk or surface hydrophobic specimens. The diffusion coefficient values are always around 10^{-4} cm^2/s, independent of the type of hydrophobic treatment, even if they are rather lower for cement paste than mortar specimens. These values are two orders of magnitude higher than those reported in the literature for water-immersed saturated cement matrices [40], but of the same order of magnitude as those cited for unsaturated cement matrices exposed to air [38,39].

It was not possible to obtain the diffusion coefficient values for non-hydrophobic specimens using the same experimental procedure, because in this case the linear trend related to oxygen pseudo-steady state diffusion was not detectable. This means that for water saturated cement paste or mortar specimens, the values of the diffusion coefficient are too low for an appreciable change in the oxygen content in the measuring compartment, and therefore undetectable by the oxygen probe.

Table 3
Oxygen diffusion coefficients for cement pastes and mortars.

	D (10^{-5} cm^2/s)		
Paste w/c	0.4	0.5	0.6
Bulk hydrophobic paste	3.0	5.4	9.1
Surface hydrophobic paste	2.4	6.1	8.0
Mortar w/c	0.5	0.6	0.7
Bulk hydrophobic mortar	12.3	12.9	22.9
Surface hydrophobic mortar	11.8	12.0	13.0

The results of the diffusion tests carried out at three different temperatures ($T = 15$ °C, $T = 25$ °C, $T = 35$ ° C) on bulk hydrophobic cementitious pastes manufactured with four different *w/c* ratios (*w/c* = 0.4, *w/c* = 0.5, *w/c* = 0.6 and *w/c* = 0.7) are reported in Fig. 5. In this figure, the logarithm of the calculated diffusion coefficients is reported as a function of the inverse of the absolute temperature. The calculated values are in good agreement with the logarithmic form of the Arrhenius equation (Fig. 5) implying that, for a given *w/c* ratio, in the temperature range considered, the kinetic of oxygen diffusion through bulk hydrophobic cementitious matrix is one step-controlled. The activation energies for oxygen diffusion through cement pastes are about 24 KJ/mol in the case of *w/c* = 0.4 and *w/c* = 0.5, while they are significantly lower (8 KJ/mol) in the case of *w/c* = 0.6 and *w/c* = 0.7. This behavior could be explained in terms of the effect of the *w/c* on the pores continuity in the material microstructure [35]. As a matter of fact, according with the classical model of Power [32], the *w/c* = 0.6 in the cement paste represents the border value that distinguishes microstructures with close porosity from those with a significant presence of open porosity, at least after 1 month of curing.

4.3. General comparison

By comparing all the results obtained for oxygen diffusion through hydrophobic cement specimens fully immersed in water (Fig. 6), it appears evident that the oxygen diffusion coefficient increases with the *w/c*, that is with the porosity of the cement matrix as already reported in the literature [37,38].

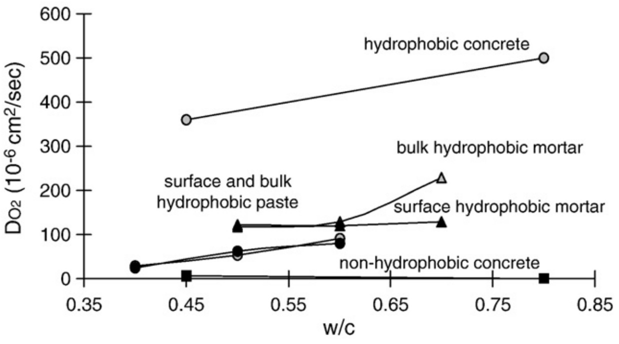

Fig. 6. Comparison between all oxygen diffusion coefficients obtained for different hydrophobic cement materials fully immersed in water with respect to non-hydrophobic concrete.

Moreover, at the same *w/c*, the oxygen diffusion coefficient increases from a more homogeneous cement matrix such as cement paste to a more heterogeneous one such as in concrete. This is probably due to preferential paths at the interfacial zone between aggregate and cement paste where oxygen can diffuse easier.

On the other hand, significant changes in the oxygen diffusion coefficient do not exist when bulk or surface hydrophobic cement specimens are tested, confirming that more and faster oxygen diffusion through fully water-immersed hydrophobic matrices, is mainly caused by unsaturation of the cement matrix.

5. Conclusions

The most important conclusion drawn from this work appears to be the oxygen diffusion coefficient value in fully water-immersed hydrophobic cement matrix which corresponds to the one reported in the literature for unsaturated cement matrix exposed to air.

The results obtained in this work seem to confirm the model proposed to explain the catastrophic corrosion found on steel plates embedded in hydrophobic cracked concrete specimens fully immersed in a chloride aqueous solution, observed previously [31]. This behavior should be related to a higher oxygen diffusion rate towards the steel reinforcement which acts as cathode through the partly empty pores of hydrophobic concrete. This concrete is hardly susceptible to water saturation and is easily crossed by the oxygen in gaseous phase stripped by the surrounding aqueous solution. In other words, the corrosion rate of the steel reinforcement close to the crack tip, in the anodic area where chloride induced corrosive attack occurs, is very high due to the hydrophobic character of the cement paste.

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