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CHLORIDE DIFFUSION THROUGH SURFACE-TREATED MORTAR SPECIMENS

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ABSTRACT

This paper reports on a study of the application of the diffusion cell method in assessing the resistance provided by surface treatments to chloride diffusion into concrete. Coatings, sealers, and penetrants were applied to 10-mm-thick mortar specimens. Chloride diffusion coefficients and chloride diffusion resistance values were calculated and compared. A silane, polymer-modified cementitious coating and polyurethane sealer gave diffusion coefficients ranging from one to over three orders of magnitude lower than the OPC mortar substrate. An acrylic sealer appeared to accelerate chloride transport. Acrylic and polyurethane coatings were too resistant for results to be available within a year of testing, but methods of accelerating the test are discussed. The influences of membrane and osmotic effects on chloride transport into surface treated concrete merit further research.

Introduction

Surface treatments are increasingly being applied to concrete structures to reduce chloride penetration from both seawater and deicing salts. In most practical situations an effective surface treatment requires resistance to both water absorption and to chloride ion diffusion, and tests are needed to measure this. Resistance to water absorption is relatively easy to measure based on gravimetrically monitoring water uptake of preconditioned specimens. Chloride diffusion resistance is more difficult to characterize, primarily because if a surface treatment is effective, natural chloride diffusion is extremely slow. Rapid indirect methods are being developed based on measuring properties expected to correlate well with chloride diffusion resistance (1,2). However, for a definitive assessment of chloride diffusion behaviour, or to calibrate an indirect method, it is necessary to undertake natural chloride diffusion testing. There are essentially two approaches, steady state and unsteady state (3).

In the unsteady state, or chloride profile method, specimens are immersed in a chloride solution for a period of months or years, and then they are analyzed and the resulting chloride profiles compared. For untreated specimens, results can be presented in the form of an apparent diffusion coefficient and a surface chloride content, based on fitting a curve to the profiles complying with the error function solution of Fick's 2nd Law. Unfortunately, this

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simple approach is unsound for interpreting chloride profiles in surface-treated specimens because the assumption of a constant boundary condition at the interface between the surface treatment and the concrete is invalid and leads to significant error (4); and there is not a mathematical model found in literature to relate profile results to the diffusion resistance of surface treatment layers. The steady state, or diffusion cell, method involves installing a thin specimen to separate half cells containing chloride and chloride-free solutions and monitoring the chloride concentration in the initially chloride-free solution as a function of time, to determine an effective diffusion coefficient. The diffusion cell method has been used widely on cementitious materials (3,5–10), but not on surface-treated cementitious materials.

This paper reports on the application of the diffusion cell method to mortar specimens treated with six different surface treatments.

Specimen Preparation

Substrate

The substrate OPC mortar used had 0.45 free water/cement ratio, and 2.5 sand/cement ratio with a maximum aggregate size of 2.36 mm. Specimens were cast as 100-mm-diameter 50-mm-thick discs. They were demoulded after 2 days sealed in the moulds and were then stored in a sealed condition at 22 ± 2°C to an age of 28 days. 10-mm-thick slices with the cast surface faces were then cut from the discs and were conditioned at 86% RH for 1 week prior to being surface treated.

Surface Treatment Materials and Application

A surface treatment can be classified as a coating, a sealer, or a penetrant. A coating can be seen as an additional dense physical layer on the concrete surface. A sealer provides a coating on the concrete surface, but also penetrates the concrete, lining or blocking pores. A penetrant (e.g., silane) penetrates the concrete, without leaving a significant surface coating. Coatings and sealers primarily act as physical barriers, whilst the most widely used penetrants line the pores of the concrete to render it hydrophoc. Table 1 gives the details of six surface treatments selected to represent the range of products available to protect concrete structures from chloride penetration. The materials were used at the coverage recommended by the manufacturers. They were applied by brush, directly onto the cast surfaces of the conditioned specimens, except for the polymer- modified cementitious coating, which was applied to a water-damped surface as required by the manufacturer’s specification. The coverage was controlled by the weight of surface treatment materials applied using an accurate (to 0.01 g) electronic balance. Treated specimens were left in open air in the laboratory at 22 ± 2°C and 50 ± 5% RH for 24 h to dry prior to further conditioning.

Conditioning of Surface-Treated Specimens

After the 24 h drying period following surface treatment, the specimens were transferred to humidity control boxes and were conditioned at 86% RH and 22 ± 2°C for 2 weeks.

In order to avoid the influence of chloride ion uptake as a result of water absorption, and

TABLE 1
Surface treatment materials and applications.

Surface treatment	Description	Coverage
Acrylic sealer	Acrylic resin based solvent borne membrane forming liquid.	0.2 L/m^2
Polyurethane sealer	Binder: hydroxy acrylic resins and aliphatic isocyanate. Solvent: aliphatic and aromatic hydrocarbons	0.12 kg/m^2
Alkylakoxysilane	Iso-butyltriethoxysilane.	0.3 L/m^2
Acrylic coating	Solvent-based pigmented methacrylate.	0.175 L/m^2 in two coats
Polyurethane coating	Hydroxy acrylates and aliphatic isocyanates.	0.35 L/m^2 in two coats
Polymer modified cementitious coating (P-m coating)	Two component acrylic modified cementitious coating.	1.8 kg/m^2

to ensure that all the specimens to be tested had the same degree of saturation, all the specimens were subjected to vacuum water saturation prior to tests. Vacuum saturation involved vacuuming the treated specimens dry for 1 h, then introducing distilled water into the vacuum chamber and maintaining the vacuum for 12 h. Finally the specimens were kept in water without vacuum for 12 h.

Diffusion Cell Testing

The diffusion cell is shown in Figure 1. The specimen separates half cells containing 1 M NaCl solution and 0.3 M NaOH solution, both saturated with Ca(OH)2. The effective area exposed to the solutions is 50.2 cm^2 and the volume of each half cell is 430 cm^3. Three replicate specimens were tested for each surface treatment at 22 ± 2°C. After the specimens were installed in the cells, the areas outside of the cell were coated with two coats of epoxy resin.

During the test, samples from the 0.3 M NaOH solution were taken regularly for determination of chloride concentration using potentiometric titration, and the solution level was maintained by adding the same volume of 0.3 M NaOH solution.

Effective diffusion coefficient, D^e, for control substrate specimens and "combined diffusion coefficient," D_c^e, for the surface treated specimens were calculated according to:

$$D = b\,\frac{VT}{C_0 A} \tag{1}$$

where b is the steady state chloride flux, i.e., the linear slope of the concentration vs. time curve obtained by curve fitting to experimental data, V the volume of the half cell, T the thickness of a control specimen or the total thickness of a surface treated specimen, C_0 the concentration of the source chloride solution, and A the area of the specimen exposed to the solutions.

In the following text, the surface treatment layer is defined as the mortar/concrete penetrated by a penetrant or sealer, plus any coating (4). After the test, the specimens were

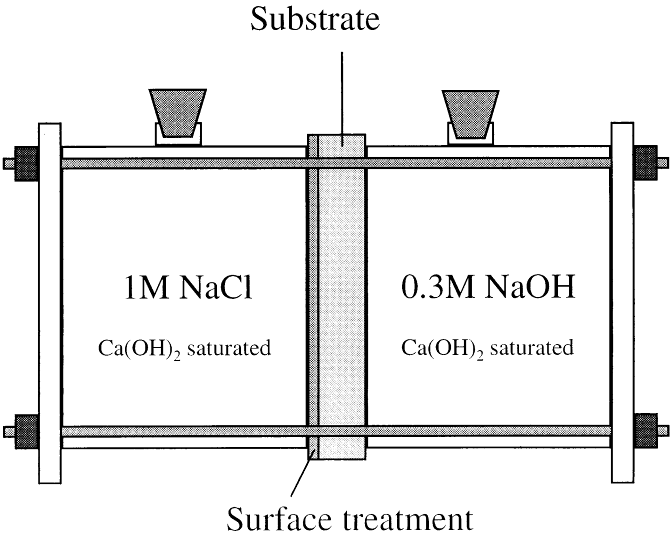

FIG. 1.
A schematic diagram of diffusion cell test setup.

dried and the thicknesses of the surface treatment layers were determined on broken sections by optical or scanning electron microscopy, after water spraying in the case of silane treatment layer. The acrylic sealer treatment layer was not visible in the microscope and had possibly degraded during the test.

Results

Table 2 presents diffusion cell test data for each replicate specimen. t_0' and b' are penetration time and penetration rate calculated for each specimen by curve fitting. t_0 and b are the averages of t_0' and b' for each set of three replicate specimens. Due to the high resistance of the acrylic and polyurethane coatings and the resultant low chloride diffusion rate, no reliable t_0 and b values were obtained.

To satisfy the requirement of steady state diffusion that the chloride concentration C in the downstream cell must be negligible with respect to the source chloride concentration C_0, the calculations of t_0' and b' for the control and acrylic sealer treated specimens were based on the data obtained over the first 100 days. For the other surface treated specimens, data obtained over the whole test period were used for curve fitting. Figure 2 shows the average experimental data of three replicates and fitted curves for the control and surface treated specimens.

The control and acrylic sealer-treated specimens exhibited a much higher chloride flux than the others. Unexpectedly, the acrylic sealer treated specimens had a higher steady chloride flux than the control specimens. Among the surface treatments tested, coatings performed better than other types of treatment.

It is interesting to note that the fitted penetration time t_0 for the control and acrylic sealer-treated specimens is very short (4.38 and −0.28 days respectively). This resulted from the fact that there were two stages of chloride penetration as observed from the control,

TABLE 2
Diffusion cell test results.

	Curve fitting results			
Surface treatment	t_0' (days)	b' (ppm/day)	t_0 (days)	b (ppm/day)
Control	1.89	11.4		
	6.31	10.9	4.38	10.7
	5.12	9.90		
Acrylic sealer	−1.69	11.6		
	0.82	11.0	−0.28	11.6
	0.06	12.1		
Polyurethane sealer	118	0.82		
	70.1	2.16	46.9	1.9
	8.14	2.79		
Silane	26.1	3.11		
	0.56	3.07	21.0	3.3
	35.1	3.33		
Acrylic coating	N/A	N/A		
	N/A	N/A	N/A	N/A
	N/A	N/A		
Polyurethane coating	N/A	N/A		
	N/A	N/A	N/A	N/A
	N/A	N/A		
P-m coating	110	1.01		
	134	1.41	1.24	1.39
	129	1.46		

acrylic sealer, and silane treated specimens. In the first stage, a higher chloride flux was estimated from the concentration vs. time curve. The second stage shows a relatively constant, but lower chloride flux.

The diffusion cells and surface-treated surfaces of the specimens were inspected regularly. It was found that the solution level in the half cell containing NaCl solution was generally higher than that in the NaOH solution. Blisters occurred in the polyurethane coating after about two weeks of testing. Figure 3 shows a SEM micrograph of a blister.

Discussion

Analysis of Test Results

The diffusion resistance R^{diff} of a specimen of finite thickness can be defined as (11,12):

$$R^{\mathrm{diff}} = \frac{T}{D} \tag{2}$$

Once chloride diffusion reaches a steady state across a surface treated specimen in a diffusion cell, the chloride concentration in the pore solution at the interface of the surface treatment layer and the substrate must be constant and the chloride flux through the surface treatment

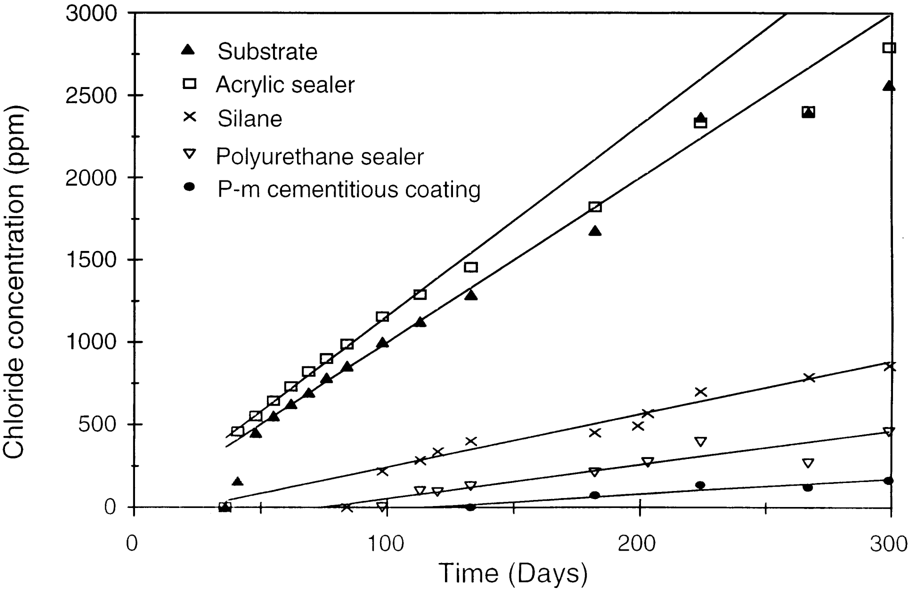

FIG. 2.
Average diffusion cell results of control and surface treated specimens.

layer and the substrate equal. Thus, applying Fick's first law to both the surface treatment layer and the substrate:

$$J = D_c^{\,e}\,\frac{C_0 - C}{T_c} = D_{st}^{\,e}\,\frac{C_0 - C_i}{T_{st}} = D_{su}^{\,e}\,\frac{C_i - C}{T_{su}} \tag{3}$$

where C_i is the interfacial chloride concentration in the pore solution, $D_{st}^{\,e}$ and $D_{su}^{\,e}$ the diffusion coefficients of the surface treatment layer and the substrate respectively, C the chloride concentration in the downstream cell, T_c, T_{su}, and T_{st} the thicknesses of the treated

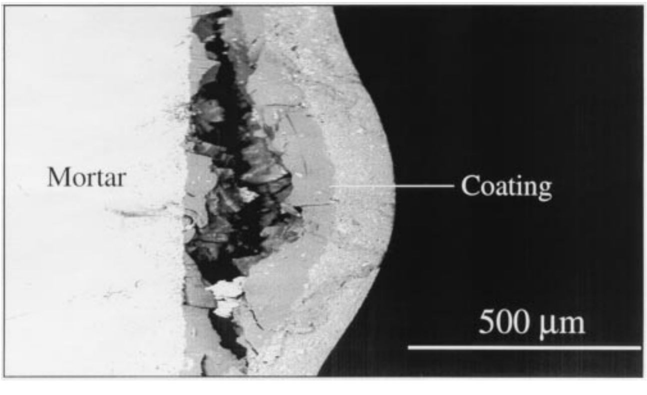

FIG. 3.
A SEM micrograph showing a blister in the polyurethane coating.

TABLE 3
Diffusion cell test results.

Surface treatment	T_{st} (mm)	T_{su} (mm)	D_c^e (10^{-12} m^2/s)	D_{st}^c (10^{-12} m^2/s)	R_{st}^{diff} (10^2 s/m)
Control	-	10	3.0	-	3.4 (substrate)
Acrylic sealer	-	10	3.3	-	-0.25
Polyurethane sealer	0.02	10	0.58	1.4×10^{-3}	21
Replicate 1	0.02	10	0.23	4.9×10^{-4}	41
Replicate 2	0.02	10	0.60	1.5×10^{-3}	13
Replicate 3	0.02	10	0.78	2.1×10^{-3}	9.5
Silane	2	8	0.58	2.5×10^{-1}	8.0
Acrylic coating	0.20	10	N/A	N/A	N/A
Polyurethane coating	0.35	10	N/A	N/A	N/A
P-m coating	1.5	10	0.42	6.3×10^{-3}	25

specimen, the substrate and the surface treatment layer respectively, and $T_c = T_{st} + T_{su}$. If $C_0 \gg C$ and rearranging equation (3):

$$\frac{T_c}{D_c} = \frac{T_{st}}{D_{st}^{e}} + \frac{T_{su}}{D_{su}^{e}} \tag{4}$$

i.e.,

$$R_c^{diff} = R_{st}^{diff} + R_{su}^{diff} \tag{5}$$

where R_c^{diff}, R_{st}^{diff}, and R_{su}^{diff} are the diffusion resistances of surface-treated specimen, surface treatment layer and the substrate respectively. Based on Eqs. 1 and 4, the diffusion coefficient of a surface treatment layer D_{st}^{e} can be calculated when the thicknesses of the surface treatment layer and the diffusion coefficient of the substrate are known.

Table 3 presents measured surface treatment layer thicknesses as an average of 10 points and calculated diffusion coefficients, D_c^e and D_{st}^e. D_c^e, D_{st}^e, and the diffusion resistance R_{st}^{diff} were calculated using t_0 and b. The diffusion coefficient of the substrate was taken as the diffusion coefficient of the control specimen, i.e., 3.0 × 10–12 m^2/s. The diffusion resistance of the acrylic sealer treatment layer is shown to be negative. The results of the three polyurethane sealer treated specimens varied significantly, probably due to uneven application which might result in microdefects (e.g., pin holes) in the coating during specimen preparation, and therefore individual results are given in Table 3 together with the average data.

Chloride Diffusion Coefficient and Diffusion Resistance of Surface Treatment Layers

Table 3 shows that the diffusion coefficients of surface treatment layers are one to over three orders of magnitude lower than that of the substrate (except for the acrylic sealer treatment), proving that the surface treatment layers are far more resistant to chloride diffusion than the substrate mortar.

D_{st}^{e} varies over three orders of magnitude among the surface treatments tested. The polyurethane sealer-treated layer had the lowest diffusion coefficient. The silane treatment layer showed a high diffusion coefficient, but this was still an order of magnitude lower than that of the substrate. Among the coatings, the P-m coating had the highest diffusion coefficient.

The thickness of the surface treatment layer varies greatly with the type of surface treatment, ranging from 20 μm for the polyurethane sealer to 2 mm for the silane. D_{st}^{e} and the thickness T of a surface treatment layer determine its diffusion resistance as calculated by Eq. 2 and listed in Table 3. Except for the acrylic sealer, all surface treatment layers show a much higher diffusion resistance than the substrate mortar (10 mm thick).

The effect of thickness of a surface treatment layer is obvious. The diffusion coefficient of the P-m coating is higher than that of the polyurethane sealer, but the diffusion resistance of the former is higher due to its greater thickness.

The diffusion resistance, taking account of thickness and diffusion coefficient, is a comprehensive and versatile quantitative parameter for evaluating the performance of a surface treatment and designing a surface treatment for a desired protective function.

Application of Diffusion Cell Test to Surface-Treated Specimens

The diffusion cell test is a simple and quantitative long-term method for studying chloride diffusion through surface-treated cementitious materials. The merit of the method is that it can measure the chloride diffusion resistance and diffusion coefficient of the surface treatment layer, giving an insight into the real performance of surface-treated concrete. The greatest drawback of the test is its long duration. For the polyurethane and acrylic coatings, the resistance of the treatments was such that the test would have had to run for several years to provide useful results. This long duration is not solely a result of the high resistance of the coatings, but is also due to the nature of the substrate. In contrast, Jones et al. (13) carried out diffusion cell tests on 5mm thick discs of sintered porous borosilicate glass with a range of surface treatments (including epoxy coatings) applied to one face and found that steady state chloride diffusion was achieved after 14 days of testing. All cements used in structural concrete bind a proportion of any chloride present and such binding is non-linear with a greater proportion bound at low concentration (14). For the more effective surface treatments, the amount of chloride diffusing into the substrate is very small, and consequently, with a cementitious substrate, during the early part of the test most of it is bound. This results in a substantial delay in significant amount of chloride reaching the downstream half cell and in steady state conditions being achieved. The short test duration achieved by using a porous glass substrate is largely a result of chloride binding being insignificant and the effective diffusion coefficient of the glass being much higher. Furthermore, Jones et al. conclude that chloride diffusion through materials applied to the glass was substantially higher than for the same materials applied to a concrete substrate. Most surface treatments interact with concrete in ways that are not replicated when applied to a glass substrate. The depth of penetration and the effectiveness of penetrants and sealers must depend upon the porosity, pore size distribution, pore continuity and in some cases the electrochemical nature of the pore walls and the composition of the pore solution. Porous glass is different from mortar/concrete in each of these respects. It is also doubtful as to whether glass is a reasonable substitute for a cementitious substrate for coatings. For example, the properties of some coatings applied to concrete deteriorate with time due to attack by the alkaline pore solution.

There are several ways that tests using a cementitious substrate could be accelerated.

1. The temperature could be raised; 40°C would not be unreasonable, as the surfaces of concrete structures in most regions where chloride penetration is a problem often reach this temperature.
2. The chloride concentration could be raised; it is not uncommon for 5 M NaCl to be used in chloride profile tests, although this would exaggerate any contribution from osmosis (discussed below).
3. The diffusion coefficient of the substrate could be increased by using a higher water/cement ratio, although a large increase would introduce the complication of the substrate pore structure not being realistic.
4. Cement with relatively low binding capacity, such as a low C_3A cement, could be used.
5. The substrate specimen thickness could be reduced. Usually, it is advisable that the thickness of concrete specimens subjected to transport tests is several times the maximum aggregate size, to reduce the impact of the low-resistance transport path along the cement paste/aggregate interface. It was for this reason that a maximum aggregate size of 2.36 mm and a substrate specimen thickness of 10 mm were used in this work. However, in this situation, it is the diffusion resistance of the surface treatment layer that is of interest and the diffusion coefficient of the substrate is not important provided replicate substrate specimens give similar results. Clearly the specimens should be thicker than potential depth of penetration of any penetrants or sealers being tested.

This work suggests that processes other than pure diffusion and chloride binding are involved in the test. The negative diffusion resistance of the acrylic sealer treatment implies that the treatment accelerate chloride transport; membrane effects (15) are a possible explanation. The blistering of the polyurethane coating and the higher water level in the NaCl solution half cell suggest osmotic behaviour. More research is needed to develop an understanding of when these processes are involved and to what extent they influence chloride transport.

Conclusions

Based on steady state diffusion theory, the diffusion cell test has been shown to be an informative approach to study chloride diffusion through surface treated cementitious specimens. In combination with thickness measurement of surface treatment layers and a control specimen test, the diffusion coefficient of a surface treatment layer and its diffusion resistance can be calculated, thus enabling different surface treatments to be objectively compared. The disadvantage of the method is that it requires a very long test time for high diffusion resistance treatments. Membrane and osmotic effects may be involved in the test, but more research is needed to develop an understanding of when these processes are involved and to what extent they influence chloride transport.

The acrylic sealer appeared to accelerate chloride transport. The silane, polymer-modified cementitious coating, and polyurethane sealer gave surface treatment layers with chloride diffusion coefficients ranging from one to over three orders of magnitude lower than the mortar substrate. The acrylic and polyurethane coatings were too resistant for results to be available after a year of testing.

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