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Modelling of Chloride Diffusion into Surface-treated Concrete

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Abstract

Chloride penetration into concrete is the main cause of the corrosion of steel in concrete structures exposed to chloride-rich environments. As a preventive or remedial method, surface treatments on concrete have been increasingly applied to both new and existing concrete structures to combat this problem. Ion diffusion is regarded as the dominant chloride transport process for structures constantly immersed in water. So far, knowledge of how a surface treatment reduces chloride diffusion is limited and the relationship between chloride diffusion resistance and surface treatment parameters, such as thickness, porosity and diffusion coefficient, has not been quantitatively identified. To gain an insight into the protective mechanism of surface treatments, a theoretical study of chloride diffusion through surface-treated concrete is required. This work proposes a unified physical model for all types of surface treatment and the concept of water-percolated porosity. The influences of surface treatment and substrate properties on chloride diffusion are studied using a finite difference model. Results indicate that chloride diffusion is controlled by both the surface treatment and the substrate. A surface treatment can significantly reduce the chloride concentration at the concrete surface, but this interfacial concentration increases with time. Hence the chloride profile in the concrete substrate does not obey Fick's law with a constant concentration boundary condition. If Fick's law is applied to such a surface-treated concrete, a diffusion coefficient, termed a pseudo diffusion coefficient, of less than the true diffusion coefficient of the substrate material is obtained.

Keywords: surface treatments, chloride diffusion, modelling, diffusion coefficient, concrete, corrosion.

INTRODUCTION

Chloride-induced reinforcement corrosion can be initiated when the chloride at the surface of rebars reaches a threshold level.[1] The time required for such corrosion initiation depends on the rate of chloride transport through the concrete cover and the external chloride concentration, with actions that reduce these parameters generally increasing this time. In this respect, the use of surface treatments can be very effective in limiting chloride transport by providing a barrier on the concrete surface.

A number of laboratory and field studies have shown that surface treatments can effectively reduce chloride transport and extend the service life of treated concrete structures.[2-4] However, little work is found in the literature in relation to studies of the protective mechanisms of surface treatments. The factors affecting chloride transport through surface-treated concrete have not been identified. Consequently, there is no sound theory that can be used to give clear guidelines for manufacturers to optimise their products or for users to select

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appropriate surface treatments. Furthermore, this lack of knowledge has also hindered the development of test methods to assess the chloride diffusion resistance of surface treatments, which has limited the development of effective surface treatments.[5] From the point of view of service life prediction, it is also essential to know how a surface treatment limits chloride diffusion and how chloride is distributed through surface-treated concrete in order to estimate the service life of a surface-treated concrete structure. Under these circumstances, a theoretical modelling study should be very helpful in elucidating the protective mechanisms of surface treatments.

The predominant mechanisms responsible for transporting chloride into surface-treated concrete depend on the exposure conditions. Chloride may diffuse through water as a result of a concentration gradient, or it may be transported by the flow of water in which it is dissolved as a consequence of capillary suction, wick action[6] or the application of a hydrostatic head. The transport coefficients governing these processes may vary with time and depth. In order to tackle such complex transport scenarios, a numerical model has been developed at Imperial College for bulk and composite two-layer systems.

The work reported here explores chloride diffusion into a surface-treated concrete without the added complications of the other processes. This is most relevant to surface-treated concrete structures immersed in water in moisture equilibrium, but also provides insights into the behaviour in other situations. The main objective is to improve the understanding of chloride diffusion into surface-treated concrete and to identify the critical factors influencing the process. Analytical solutions of Fick's law for composite systems comprising two layers of different diffusion coefficient have been derived[7] and have been used to study the effect of the surface skin of concrete.[8] Diffusion with time-dependent surface concentration and diffusion coefficients in a single medium have been modelled too.[9] However, in surface-treated concrete, there is usually a major difference between the porosity of the surface treatment layer and the concrete substrate, and this would be expected to have a critical influence on chloride diffusion. For this reason, the existing analytical solutions are not appropriate and the finite difference method was adopted in this study.

PHYSICAL MODEL

Surface treatments can be classified into three groups as shown in Fig. 1: (a) coatings, (b) penetrants and (c) sealers. A coating can be seen as an additional physical layer on the concrete. A penetrant (e.g. silane) penetrates the concrete, lining or blocking pores without leaving a significant surface coating. A sealer acts as both a coating and a penetrant. For penetrants or sealers, the concrete layer impregnated by the surface treatment material can be regarded as equivalent to a coating on the underlying untreated substrate concrete which therefore has a reduced thickness. Hence all surface treatments can be regarded as *surface treatment layers* as shown in Fig. 1(d). Once the surface treatment has been penetrated, chloride continues to be transported farther into the cover.

Because the transport of chloride ions is waterborne, there are two prerequisites for chloride diffusion to take place in both the surface treatment layer and the concrete substrate: (1) the presence of water and (2) continuous water paths.

The water in a surface treatment layer can be sourced from external water in contact with the layer, from the substrate concrete or from the condensation of water vapour. The water paths can take many forms depending on the surface treatment group, material type and environmental conditions. In polymer coatings or sealer-treated concrete layers, water and vapour may diffuse into the polymer materials.[10] This water may form continuous paths for chloride diffusion. For penetrant-treated layers, water can penetrate by capillary absorption if the treated layer is not fully hydrophobic or by water vapour diffusion. Needless to say, defects such as pinholes and cracks are possible water paths. Not all the pores can be occupied by water and neither do all the water-filled paths contribute to chloride diffusion. As shown in Fig. 1(d), only the water-percolated paths contribute. Therefore, it is necessary to define the volume fraction of water-percolated paths (based on the whole volume of the surface treatment layer) as the *water-percolated porosity*, P_{st}, of a surface treatment. Similarly, we define the water-percolated porosity of the substrate, P_{su}.

The value of P_{st} is related to the external environment, e.g. water pressure or relative humidity (RH). However, given a particular environment, it should depend on the intrinsic properties of the surface treatment layer and it can be one of the criteria in assessing the chloride diffusion resistance of a surface treatment. The advantage of using P_{st} is that it distinguishes itself from total porosity, much of which may not contribute to chloride diffusion. It is apparent from the definition that high total porosity or high vapour permeability does not necessarily indicate a high P_{st}. For example, a silane treatment may not change the total porosity of the concrete treated,[11] but may significantly reduce P_{st}. For simplicity, the term porosity will be used in this work to refer to P_{st} or P_{su} unless otherwise specified.

In the context of this study, other important characteristics of a surface treatment layer are its chloride diffusion coefficient, D_{st}, and thickness, T_{st}. These two parameters together with P_{st} will be used to characterise a surface treatment layer. The values of P_{st}, D_{st} and T_{st} may be interdependent. However, for simplicity of interpretation, the parameters are considered independently.

When two porous materials are joined, there may be a physical mismatch of their pore structures or a thin interfacial layer formed as a result of chemical interactions between the two materials such that there is an interfacial resistance, i.e. a bottleneck to transport at the interface. In the case of impregnated surface treatment layers, produced by either penetrants or sealers, this effect is unlikely to occur since the porosity would be continuous from the surface-treated layer into the concrete. In the case of coatings, a mismatch may be envisaged, but the authors could not find any information on this effect in the literature. If a coating were applied to a cut surface of concrete made from a very dense aggregate and there was excellent adhesion, it would be expected that there would be interfacial resistance at the coating/aggregate interface. However, in practice it is very rare to

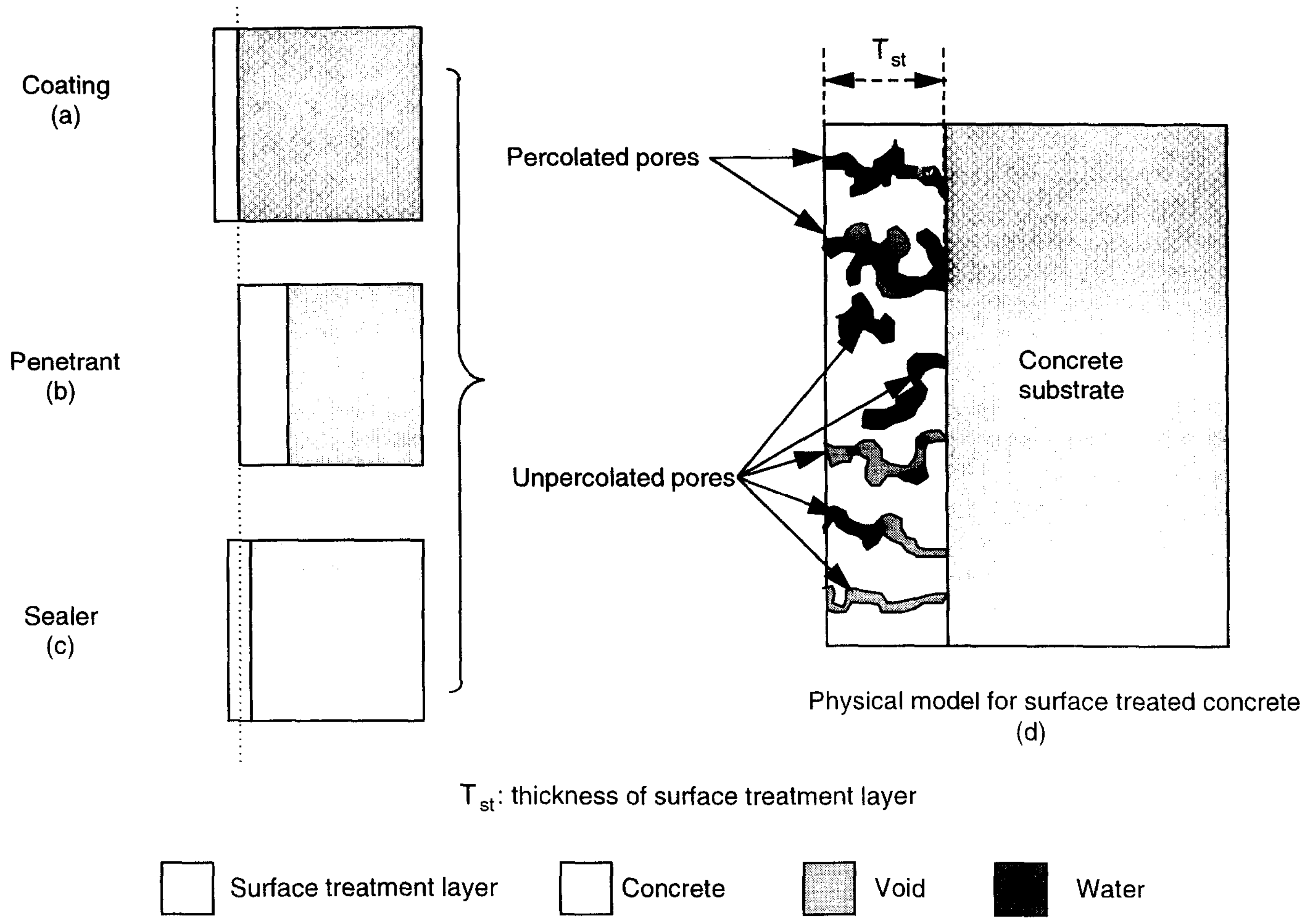

Fig. 1. Physical model for chloride diffusion through surface-treated concrete.

apply a coating to a cut surface. Coatings are usually applied to as-cast/finished surfaces where the surface is almost entirely cement paste. Cement paste has a porosity of at least 30% and the pores are fine (typically 2 nm to 1 μm), but large enough to support chloride ion diffusion; in this case the interfacial resistance may be small. It is difficult to estimate the likely scale of the effect without having detailed information concerning the pore structure of the particular coating, the concrete substrate and the interface between them. To investigate further the resistance of surface-treated concrete to chloride diffusion, the authors measured impedance spectra for mortar specimens treated with one of five commonly used coatings and sealers.[12] The impedance spectra consisted of two individual spectra located at medium and high frequencies, and these could be attributed to the different dielectric properties of the surface treatment materials and cementitious substrate, respectively. There was no evidence of a significant interfacial resistance. With this background, it was decided not to include interfacial resistance as a component of the model.

All cements bind a proportion of the chloride present, effectively removing it from the pore solution, with a greater percentage of chloride bound at lower chloride levels.[13] It is likely that some surface-treated layers also bind chloride. Chloride binding affects chloride ingress by removing some chloride from the transport process and by changing the concentration of the solution in the pores, and therefore the concentration gradients driving ionic diffusion. The net effect is to slow down the chloride transport process. The authors are not aware of any measurements of chloride binding by surface-treated layers and there is very little data in the literature concerning chloride binding at the very low chloride levels that are found to exist in the concrete substrates of effective surface treatment layers. Furthermore, at least two variables are required to describe a chloride binding relationship.[13] Hence to involve binding in both the surface treatment layer and the substrate would require at least four extra variables and the values assigned to them would have to be guessed. Consequently chloride binding was not modelled specifically in this work. However, all of the results were reviewed with regard to the qualitative effect that binding would have and the conclusions are all valid whether or not binding occurs.

FINITE DIFFERENCE MODEL

Surface-treated concrete can be modelled mathematically as a thin layer (surface treatment layer) in contact with a semi-infinite medium (concrete substrate). Chloride profiles are expressed as free chloride concentration (mol l^{-1}) of the pore solution.

Fick's law is used to describe diffusion:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{1}$$

with the initial condition:

$$C = 0, t = 0, x > 0 \tag{2}$$

and boundary conditions:

$$C = 0, x = \infty \tag{3}$$

$$C = 0.5\ \mathrm{M}, x = 0, t \geq 0$$

0.5 M chloride concentration is chosen to approximate sea water and it is assumed that this is the chloride concentration of the pore solution at the exposed surface of the surface treatment layer.

To model chloride transfer across the surface treatment layer/concrete interface, the following conditions are applied at $x = T_{\mathrm{st}}$:

$$P_{\mathrm{st}}D_{\mathrm{st}}\left.\frac{\partial C}{\partial x}\right|_{\mathrm{st}} = P_{\mathrm{su}}D_{\mathrm{su}}\left.\frac{\partial C}{\partial x}\right|_{\mathrm{su}} \tag{4}$$

$$C_{\mathrm{st}} = C_{\mathrm{su}}$$

An explicit finite difference method has been used to create approximate solutions to eqn (1) whilst implementing the initial condition (2) and boundary conditions (3) and (4). This is achieved by replacing the differential terms in eqns 1, 3 and 4 by first- and second-order Taylor expansions. The chloride concentration in the pore solution may then be calculated throughout the surface treatment layer and the substrate concrete at discrete points in time and space. The positioning of these points is determined by several requirements. First, in order to incorporate the boundary condition (4), a solution point is positioned on the interface between the surface treatment layer and concrete substrate. Second, stability of the solution mechanism must be fulfilled in the surface treatment layer where the resolution of the solution points in space is highest. Stability is defined by the criterion:

$$\frac{kD}{h^2} \leq \frac{1}{2}$$

where k is the time between adjacent time points and h is the space between adjacent space points. Once the geometry of the solution points is established in the surface treatment layer, the dimensions are reproduced in the concrete substrate. To ensure stability the space between adjacent space points should be maximised. Although stable, this tends to produce an inaccurate approximation owing to the truncation error in the Taylor expansions. A third requirement for the positioning of the solution points is determined by this trade-off between accuracy and stability. Accuracy is difficult to quantify given the lack of an exact solution, although an idea of the level of convergence can be obtained by simply running a stable model with decreasing h and determining the error between successive runs of increasing accuracy. Another method is to compare the approximate solution to a known analytical solution using a simplified environment, say one where porosity is invariant.[7] The difference between the approximation and exact results can indicate the accuracy of the approximation in the more complex environments of interest. Both tests have been undertaken for the work presented here, and all results presented are chosen so as to ensure that any inaccuracy resulting from the solution method is negligible.

The default values of parameters used in the following calculations are as follows, unless indicated otherwise in the graphs.

D_{st}: diffusion coefficient of surface treatment layer, 10^{-12} m^2 s^{-1}.
D_{su}: diffusion coefficient of bulk substrate concrete, 10^{-11} m^2 s^{-1}.
T_{st}: thickness of surface treatment layer, 0.001 m.
T_{su}: thickness of substrate used in finite difference analysis, 0.05 m.
P_{st}: water-percolated porosity of surface treatment layer, 0.01.
P_{su}: water-percolated porosity of substrate concrete, 0.2.
t: exposure time, 3.15×10^7 s (1 year).
C_0: external chloride concentration, 0.5 M.

In practice, the D and P values may vary with time due to varying moisture content, leaching of pore solution ions, further hydration and degradation of surface treatment layers. The model could allow input of such variations, but there are insufficient data available to justify using anything other than time-constant values.

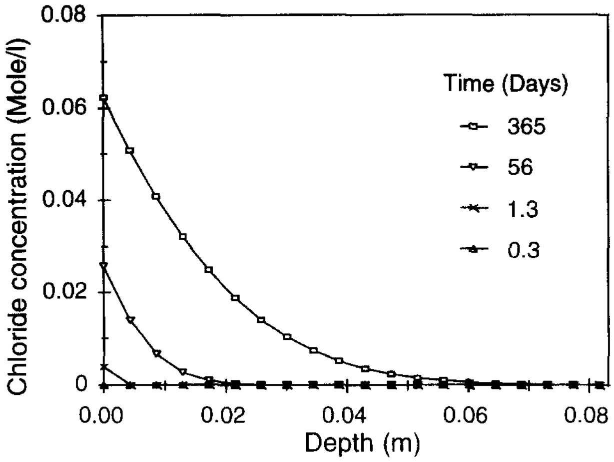

Fig. 2. Chloride concentration profiles in a surface-treated concrete substrate.

RESULTS AND DISCUSSION

Chloride concentration profiles in surface-treated concretes

Figure 2 shows profiles in a surface-treated concrete substrate at different times and Fig. 3 gives the corresponding profiles in the surface treatment layer. It can be seen that chloride ions penetrate through the surface treatment layer in the first few days and then the profile in the surface treatment layer becomes linear instead of having a typical error function shape. After chloride penetrates through the surface

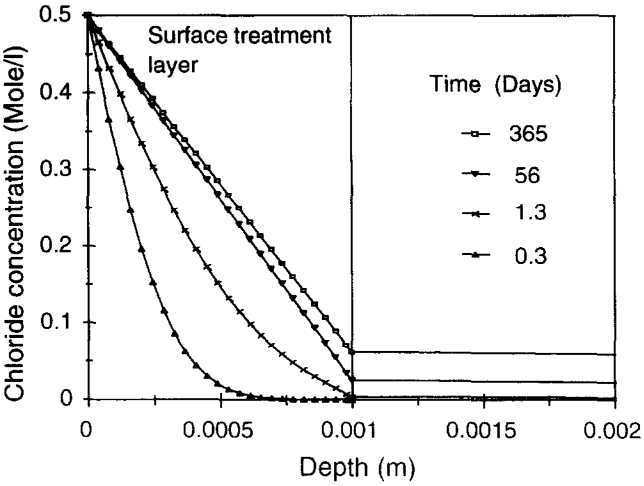

Fig. 3. Chloride concentration profiles in surface treatment layer.

treatment layer, the interface chloride concentration, C_i, increases with time. The concentration gradient in the surface treatment layer decreases with time because of the continuous increase of C_i. Since the porosity and diffusivity in the substrate are higher than those in the surface treatment layer, the profile in the substrate has a much lower concentration gradient. If the profiles are expressed in terms of chloride by weight of surface treatment and concrete, there is a step up in chloride content when moving from the surface treatment layer to the concrete owing to the higher porosity, and hence greater pore solution volume, of the concrete than the surface treatment layer.

It is noteworthy that the time to reach a linear profile in a surface treatment layer is relatively short, even though the diffusion coefficient of the surface treatment layer is an order of magnitude lower than that of the substrate concrete.

Effects of surface treatment parameters on interface concentration, C_i

The profiles in the surface treatment layer and the substrate are related by the interface concentration, C_i. As shown in Fig. 4, C_i increases sharply with time over the early period. As the degree of chloride saturation of the substrate increases, the rate of increase of C_i reduces.

Figures 5–7 show that C_i increases with increases in D_{st} and P_{st} and with a decrease in T_{st}. It is interesting to note that P_{st} has a comparable effect on C_i to D_{st}, implying that water-percolated porosity is an important parameter in controlling chloride diffusion. Any methods which reduce P_{st} and D_{st} (these include aspects of surface treatment formulation and good workmanship, but may also include substrate drying) will be particularly

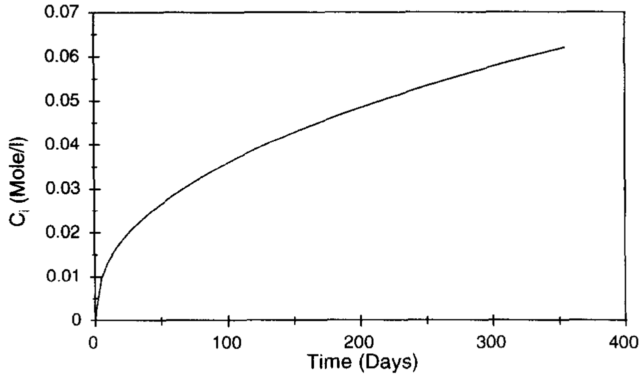

Fig. 4. Interface concentration, C_i, as a function of time.

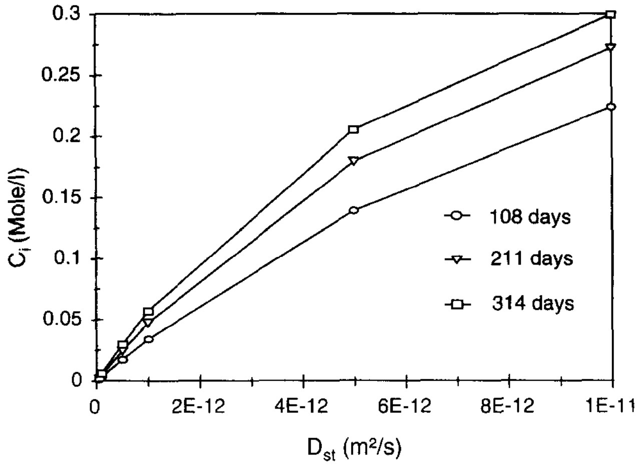

Fig. 5. Interface concentration, C_i, as a function of D_{st} and time.

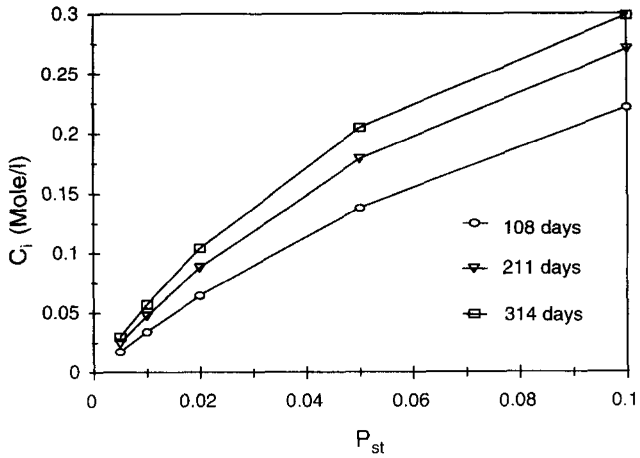

Fig. 6. Interface concentration, C_i, as a function of P_{st} and time.

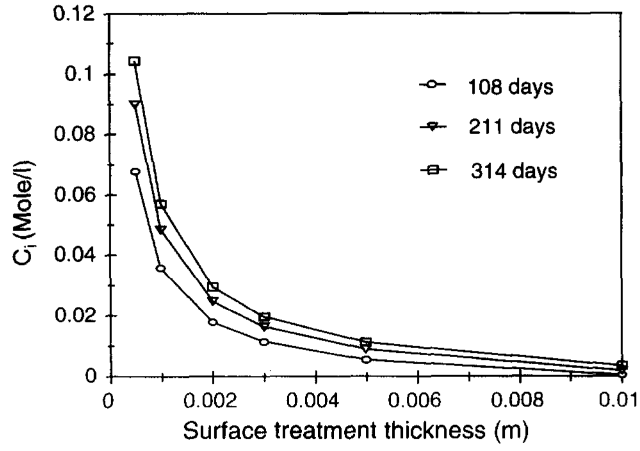

Fig. 7. Interface concentration, C_i, as a function of T_{st} and time.

effective at increasing resistance to chloride diffusion.

Once the profile in the surface treatment becomes linear, eqn (5) applies:

$$J_{Cl} \propto P_{st} D_{st} \frac{C_0 - C_i(t)}{T_{st}} \tag{5}$$

The chloride flux, J_{Cl}, is proportional to P_{st} and D_{st}, and inversely proportional to T_{st}. Both low D_{st} and low P_{st} limit the chloride flux into the substrate and high thickness reduces the chloride concentration gradient in the surface treatment layer. From the standpoint of the concrete substrate, diffusion into the substrate can be approximated as a time-dependent boundary problem. In comparison to untreated concrete, the chloride concentration at the surface of the concrete is significantly reduced by the application of a surface treatment.

Effects of concrete substrate parameters on interface concentration, C_i

Figure 8 shows the dependence of chloride profiles on the substrate porosity, P_{su}, and Fig. 9 gives the dependence of C_i on P_{su}. The porosity in the substrate can significantly reduce the interface concentration, C_i. This is because as chloride diffuses through the interface it is diluted by the large volume of pore solution in the substrate.

Figure 10 shows profiles for substrates with different diffusion coefficients. It is interesting to note that substrate concrete with a lower diffusion coefficient leads to a higher chloride concentration in the area near the surface treat-

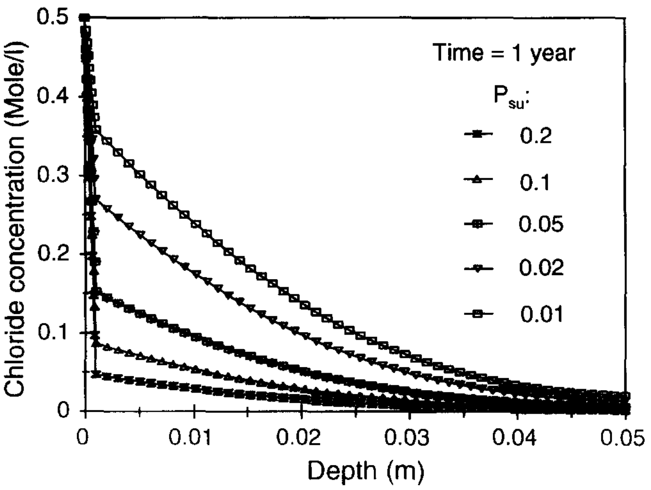

Fig. 8. Chloride concentration profiles in the substrate as a function of P_{su} after 1 year.

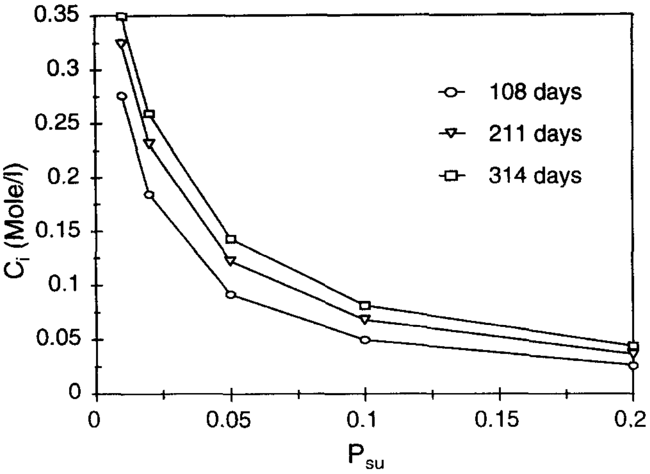

Fig. 9. Interface concentration, C_i, as a function of P_{su} and time.

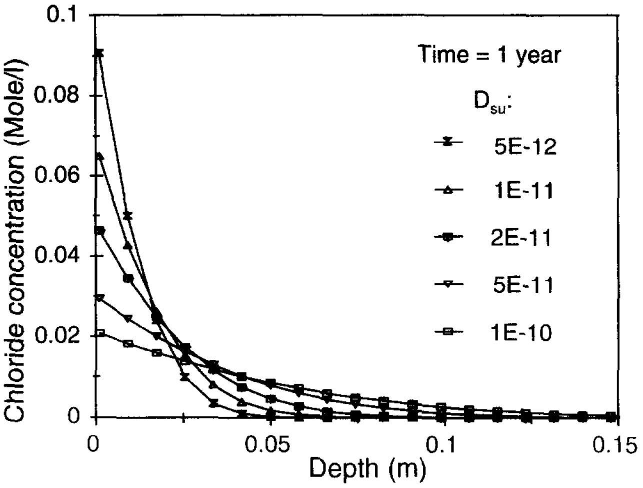

Fig. 10. Chloride concentration profiles as a function of D_{su} after 1 year.

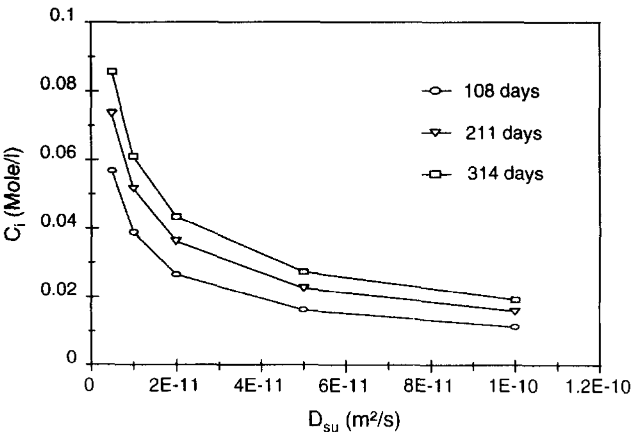

Fig. 11. Interface chloride concentration, C_i, as a function of D_{su} and time.

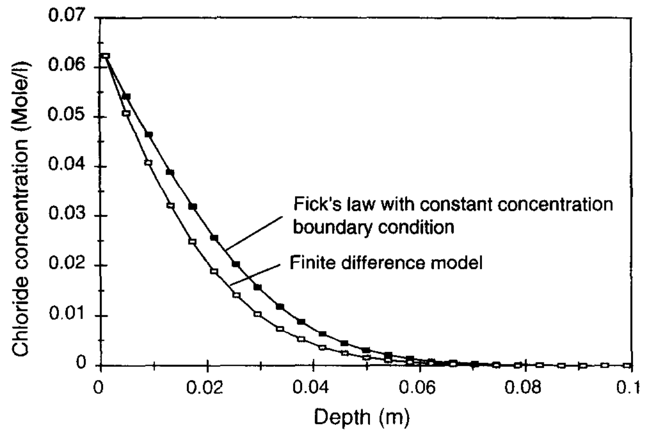

Fig. 12. Comparison of profiles obtained from Fick's law and finite difference model (after 1 year).

ment, but a lower concentration at greater depth. In terms of penetration depth, the substrate with a high D_{su} has deeper chloride penetration. From the point of view of corrosion initiation, a rebar located near the surface treatment in a low-diffusion-coefficient concrete may have a higher corrosion risk than in a poor-quality substrate. However, a poor-quality concrete with a high diffusion coefficient would suffer deeper chloride penetration.

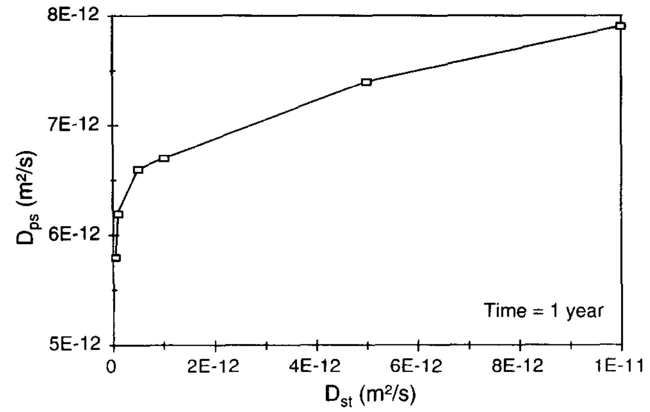

Fig. 13. Pseudo diffusion coefficient, D_{ps}, as a function of D_{st} after 1 year.

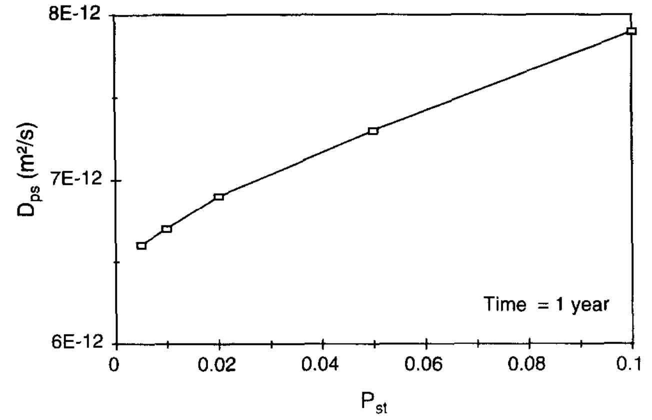

Fig. 14. Pseudo diffusion coefficient, D_{ps}, as a function of P_{st} after 1 year.

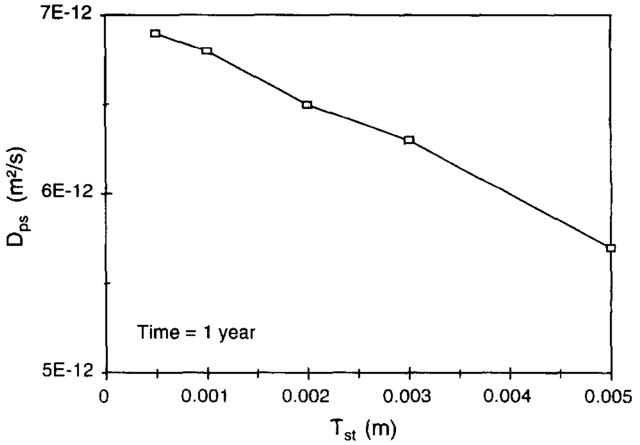

Fig. 15. Pseudo diffusion coefficient, D_{ps}, as a function of T_{st} after 1 year.

The results demonstrate that a poor-quality substrate concrete (high P_{su} and D_{su}) results in a lower value of C_i as shown in Figs 10 and 11. This is because high D_{su} allows chloride ions to diffuse to a greater depth, reducing the chloride concentration level in the substrate, and high P_{su} dilutes the chloride diffusing from the surface treatment layer. These effects lead to a low C_i, which consequently facilitates chloride penetration through the surface treatment layer, and hence a poor-quality substrate not only has a low resistance to chloride diffusion, but can also accelerate chloride diffusion through surface treatments. This implies that applying the same surface treatment to different quality concretes will give different overall performance. Therefore, it is important that a surface treatment assessment should be based on the same substrate and that a comparison of surface treatments should take the quality of the substrate into account.

Pseudo diffusion coefficient in surface-treated concrete substrate

The concentration profile in the substrate is important in terms of service life prediction. Figure 12 shows a comparison of profiles in a substrate calculated by the finite difference model and by Fick's second law with a constant boundary condition in which the value of C_0 is replaced by C_i. It is clear that the two concentration profiles are different. This discrepancy results from the time dependence of C_i. When

Fick's second law with a fixed boundary concentration condition is applied to the profile in the substrate, the chloride diffusion coefficient is underestimated.

Because of difficulties associated with analysing thin surface treatment layers to abstract information regarding chloride diffusion, chloride profiling in the substrate concrete is always a preferred method of examining surface treatment performance. Therefore, despite the fact that the profile is not a function described by Fick's second law with a fixed boundary concentration, it is still useful to calculate the diffusion coefficient which is termed here the *pseudo diffusion coefficient*, D_{ps}, to differentiate it from the true diffusion coefficient, D_{su}, calculated from untreated control substrate concrete. It is clear that D_{ps} is always lower than D_{su} if $D_{st} < D_{su}$.

It is very difficult analytically to relate D_{ps} to the parameters of a surface treatment and to the true diffusion coefficient of the substrate, D_{su}. Here only comparisons are given to demonstrate the effects of surface-treated concrete parameters on D_{ps}. Figures 13–15 show the dependence of D_{ps} on the surface treatment parameters. D_{ps} decreases with an increase in T_{st} and with decreases in P_{st} and D_{st}. Therefore, it can be concluded that the more effective a surface treatment is, the lower D_{ps} is.

CONCLUSIONS

1. A physical model and a finite difference model have been established which can be used to investigate theoretically the effects of different variables on chloride diffusion into surface-treated concrete.
2. Chloride diffusion into surface-treated concrete is controlled by both the surface treatment and the substrate. Interface concentration, C_i, increases with increases in the diffusion coefficient of the surface treatment, D_{st}, water-percolated porosity, P_{st}, and time, and decreases with increases in the diffusion coefficient of the concrete substrate, D_{su}, water-percolated porosity, P_{su}, and the thickness of the surface treatment layer, T_{st}.
3. The pseudo diffusion coefficient, D_{ps}, calculated from the profile in a substrate using a fixed concentration boundary condition is lower than the true diffusion coefficient, D_{su}. Reducing P_{st} or D_{st} or increasing T_{st} decreases D_{ps}.
4. The water-percolated porosity, P_{st}, is an important factor in controlling chloride diffusion into a surface-treated concrete. Decreasing P_{st} can reduce chloride diffusion as effectively as reducing D_{st} or increasing T_{st}.

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