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Effect of initial curing on chloride diffusion in concrete repair materials

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Abstract

This paper presents the results of an experimental investigation on the effect of initial curing on chloride diffusion in three generic repair materials and a concrete mix of similar grade. Two field conditions of initial curing were simulated as follows: (1) exposure to a chloride environment after 24 h of casting to simulate repair situations, for example in the tidal zone of marine structures where repairs cannot be protected from tidal exposure for long periods; and (2) 28 days of curing at 20°C, 55% relative humidity to simulate field conditions where the repair patches are exposed to the ambient environment without any prolonged protected curing. For comparison purposes identical specimens were cured in water at 20°C for 28 days before exposure to the chloride environment. Chloride concentration profiles in the materials were determined after 28, 90, and 180 days of exposure. Regression analysis of the experimental data was carried out applying Fick's second law of diffusion to determine the diffusion coefficients (D_C) and chloride concentration on the surface (C_0). Based on the results obtained, an analytical expression for the long-term prediction of chloride concentration in repair materials is given. The results show a high rate of chloride diffusion in the cementitious repair materials containing polymer latex additives relative to plain concrete. The effect of inadequate initial curing on chloride penetration (e.g., exposure to chlorides after 24 h of casting or 28-day air curing) is more pronounced in concrete mixes than in generic repair materials. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Curing; Diffusion; Permeability; Chloride; High performance concrete

1. Introduction

Chloride-induced corrosion of reinforcement is one of the major causes of deterioration in reinforced concrete structures [1,2]. Structural members damaged by corrosion are often reinstated by applying repair patches. Repairs, however, are successful in the long term only if the causes of the original damage have been understood and appropriate repair materials are applied to resist future deterioration. The repair material should have suitable properties required to form an effective physical and chemical barrier against the penetration of deleterious substances, such as chlorides and carbon dioxide. Initial curing to which a repair is subjected prior to exposure to a chloride environment plays an important role in determining the chloride penetration rates into the repair material [3]. In practical situations, it is often impossible to provide ideal conditions of initial curing (high humidity, normal temperature over a long period of time, e.g., 28 days) to repair patches. The effectiveness of curing compounds is usually uncertain; repair patches are frequently applied to structures located in hot, arid climates and indeed in some situations (e.g., repairs to marine structures in the tidal zone) repair patches are exposed to seawater within a few hours of application. Consequently, a knowledge of the chloride penetration characteristics of inadequately cured repair materials is important for the effective design and selection of concrete repair solutions. Concrete repair formulations often contain special constituents (e.g., polymer latex modifiers) that can significantly influence the effects of initial curing with respect to chloride penetration. These characteristics need to be quantified.

Drying of cementitious materials due to poor curing, particularly at the surface, leads to restricted hydration in the surface layers and thus to higher porosity and permeability [4]. This can result in rapid chloride penetration. On the other hand, an initial period of moist curing that is followed by rapid drying can lead to cracking of the concrete surface [5]. These cracks form major flow paths for chloride penetration. In cracked and uncracked sections alike, chloride ions diffuse through capillaries and voids within the matrix and along cracks in the aggregate particles and along the interface of coarse aggregates [6]. A study on precracked marine concrete concluded that chloride concentrations in the vicinity of cracks are not significantly affected at crack widths less than 0.2 mm. Crack widths greater than 0.5 mm,

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however, lead to marked increase in chloride concentration in their vicinity [7,8].

2. Methods

2.1. Materials and mixes

Three generic repair materials (A, B, and C) that are produced commercially were used together with a plain concrete mix of similar grade. These materials were supplied as single component systems, ready for on-site mixing with the addition of potable water.

2.1.1. Material A

Material A is a blend of Portland cement (PC), graded aggregate of nominal size (5 mm) and additives that impart controlled expansion in both the plastic and hardened state while minimising water demand. This high performance nonshrinkable material can be used for the reinstatement of concrete. The manufacturer's recommended water content of 13.0% by weight of the material was used.

2.1.2. Material B

Material B is a proprietary mineral-based material with no coarse aggregate size particles or additives. It is relatively porous to allow continuous leaching of salts from contaminated concrete after the application of repair. The water content used was 16.0% by weight of material, as per manufacturer's recommendation.

2.1.3. Material C

Material C is a single-component cementitious mortar containing microsilica, nonmetallic fibre reinforcement, and styrene acrylic copolymer. The thixotropic nature of the product allows ease of application in voids, rendering and reprofiling vertical and horizontal surfaces. The recommended water content used was 16.0% by weight of material.

A plain concrete mix was used as control for comparison purposes containing PC to BS12: 1996, fine aggregate conforming to Zone M of BS882 and coarse aggregate of 10-mm maximum size. The mix proportions (by weight) were 1:2.24:3.22 with the cement content 343 kg/m^3 and water/cement ratio of 0.56.

The grading curves of the repair materials [9] show that material A is much coarser than materials B and C. It contains a significant volume of aggregates of particle size 1.18 mm or greater. Repair materials B and C are of similar grading, with particle size much smaller than 1.18 mm. The concrete mix is much richer is coarsely graded particles of 10-mm maximum size.

2.2. Preparation of test specimens and initial curing

The repair materials were mixed thoroughly in the dry state until a uniform consistency was attained; water was then added slowly and mixing was continued until a uniform mix was achieved. Prism specimens were manufactured in two series (Series 1 and 2) for the chloride diffusion investigation. After casting, all the specimens were covered with a polythene sheet and stored in the laboratory air (typically at 18–20°C, 50–55% relative humidity) for 24 h and subsequently demoulded.

After demoulding for Series 1, twelve prism (100 × 100 × 300 mm) specimens of each material were cured in one of the following two conditions for 28 days prior to exposure to chloride environment:

1. Continuous air curing at 20°C, 55% relative humidity
2. Continuous water curing at 20°C

Following this initial curing, five faces of each prism were sealed with a bituminous paint in order to ensure that chloride penetration occurred only from one unsealed longitudinal face of the prism. The coated specimens were left in the laboratory air for 2 days to allow the bituminous paint to fully harden. Specimens were than immersed in a sodium chloride solution of 3 M/L concentration (175 g of NaCl per L of water), which was maintained at 20°C. The concentration of this chloride solution was higher than seawater in the North Sea (0.6 M/L) and similar to seawater used in the laboratory spray chambers which, due to evaporation, had a range of chloride concentration 1 to 4 M/L [10]. The immersion period in the chloride solution was up to 180 days.

In Series 2, six prisms (100 × 100 × 500 mm) of each material (A, B, C, and concrete) were cast. Sealing of the specimen faces with the bituminous paint was not adopted in this case due to the early (24 h after casting) exposure to a chloride environment. Instead, during casting, polythene sheeting was carefully located as shown in Fig. 1 to provide a barrier against chloride penetration, except from one longitudinal face of each test specimen.

2.3. Chemical analysis

After the required period of immersion in the chloride solution (28, 90, 180 days), two prism specimens were taken out of the tank. They were wet-cut into two halves by a masonry saw, as shown in Fig. 2. Powder samples for chloride analysis were drilled perpendicularly to each of the sawed faces at various depths from the unsealed face as shown in Fig. 3. Drilling into each half of a specimen was performed by means of a rotary percussion drill at a distance of 10, 20, 30, 40, and 50 mm from the unsealed surface to the centre line of the drilled holes (Fig. 3). At 10 mm from the unsealed surface, five holes of 4-mm diameter and at all other positions three holes of 6-mm diameter were dry-drilled. The holes were drilled to a depth of 30 mm. At each test age the total powder sample at a common depth from the surface was obtained by combining the drilling obtained from the four cut faces of the two prism specimens. The total combined weight of the powder at each depth was up to 20 g. The sampling procedure was in accordance with BS1881: Part 124; 1988. The powder sample of drillings from each depth was mixed thoroughly and then sieved on a

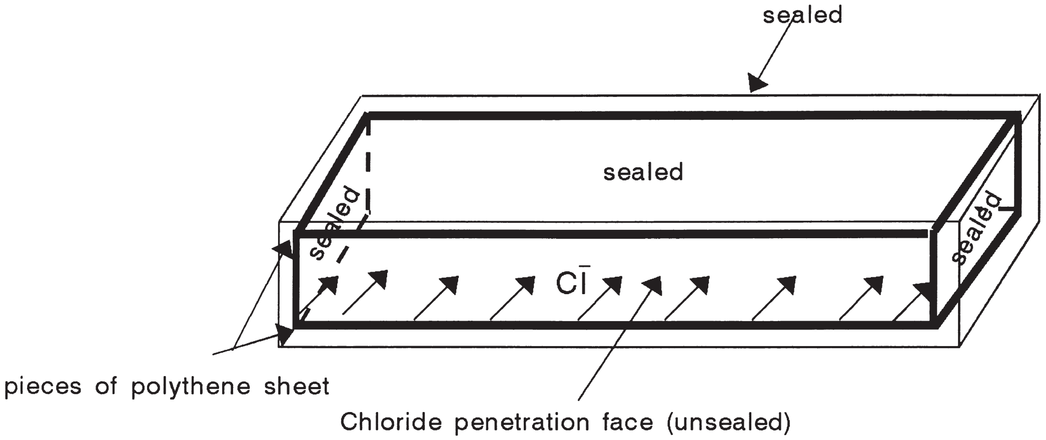

Fig. 1. Sealing of specimens of Series 2 tests exposed to salt solution 24 h after casting.

150-μm sieve. Four representative samples of 2 g each were then measured accurately to the nearest 0.01 g for use in chemical analysis. Nitric acid (20 mL of 0.1 M) was added to the sample and the mixture was heated on a hot plate for 1 min while stirring continuously. This process ensured the extraction of chloride from the powder. The solution was left to cool down. On cooling this solution was neutralised, filtered, and the Mohr titration carried out to determine the concentration of chloride in the solution [11].

The percent chloride, by weight of the concrete or repair material, was determined from Eq. (1) [12]:

$$\%\mathrm{Cl}^- = \frac{35.453\ V\ N}{10w} \qquad (1)$$

where V is the volume of $AgNO_3$ (mL) used to neutralise Cl^-, N is the normality of $AgNO_3$, and w is the weight of the powder sample in grams.

The chloride concentration determined by the above analysis is termed as acid-soluble chloride, which includes chemically bound chloride in the matrix. The chloride concentration at each depth given in the paper is an average value of four samples obtained from four cut faces of two prisms at each age (28, 90, and 180 days).

3. Results and discussion

3.1. Properties of the repair materials

The basic properties of the materials under standard water curing (at 20°C) are given in Table 1 [9]. Repair material A and concrete have similar fresh densities but the 28-day strength of material A is much higher. Repair material B has a low density, low strength, and high permeability. Material C has a lower density than concrete but the strength is slightly higher. The permeability coefficient is lowest for materials A and C, followed by the control concrete mix. Material B has by far the highest permeability coefficient.

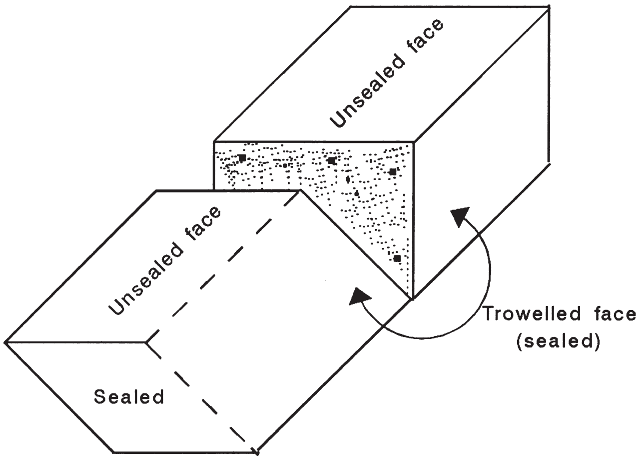

Fig. 2. Specimen cut in half to extract powder samples.

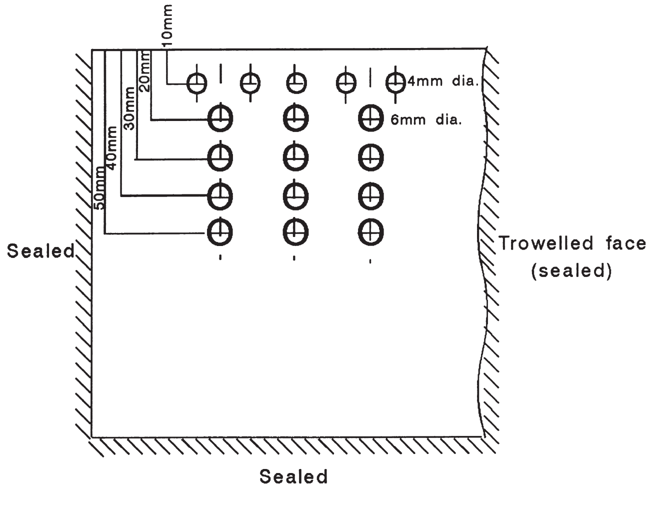

Fig. 3. Powder sample locations.

Table 1
Properties of repair materials A, B, and C and concrete

Material	Fresh density (kg/m^3)	Compressive strength, 28 days (N/mm^2)	Permeability coefficient*, 28 day (m/s)
A	2069	63.7	2.5×10^{-13}
B	1575	33.0	5.6×10^{-11}
C	1700	44.1	1.3×10^{-13}
Concrete	2100	41.0	1.1×10^{-12}

* Coefficient of water permeability using Darcy's law [9].

The coefficient of water permeability under constant flow was calculated using Darcy's Law at 28-days age [9]. In addition to the properties listed in Table 1, it has also been established that the creep and shrinkage/expansion deformations of material C are much greater than the other materials [9]. These results indicate the strong influence of the styrene acrylic polymer addition on the properties of material C. Detailed information of the physical and mechanical properties of these materials is given elsewhere [9].

3.2. Chloride diffusion profiles

3.2.1. Initial curing: 24 h in the mould

The chloride diffusion profiles of repair materials A, B, C and concrete, which were exposed to a chloride environment after 24 h of casting, are shown in Fig. 4. The chloride contents at different depths from the exposed surface were determined after 28, 90, and 180 days of exposure to a chloride environment. The experimental data points are represented by different symbols for each age of exposure. A regression analysis of the experimental data was carried out based on Fick's second law of diffusion, whose standard solution is given by Eq. (2) [13]:

$$C_{(x,t)} = C_0\left[1 - erf\left(\frac{x}{2\sqrt{D_c t}}\right)\right] \tag{2}$$

where, x = distance from concrete surface (cm); t = time (seconds); D_c = diffusion coefficient (cm^2/s); C_0 = equilibrium chloride concentration on concrete surface; $C_{(x,t)}$ = chloride concentration at position x; time t; and erf = error function.

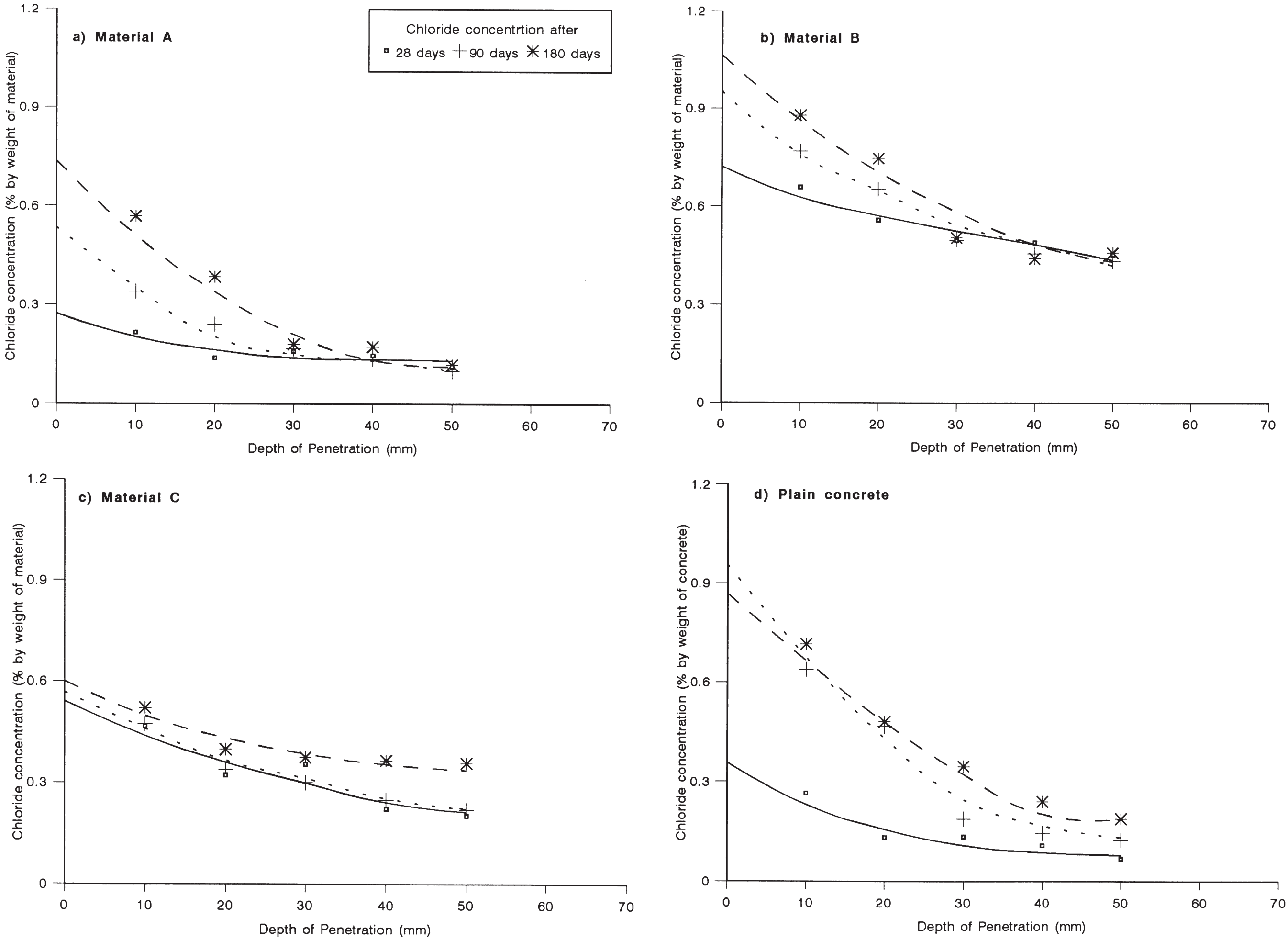

Fig. 4. Chloride diffusion profiles for (a) material A, (b) material B, (c) material C, and (d) concrete. Initial curing: 24 h in the mould after casting.

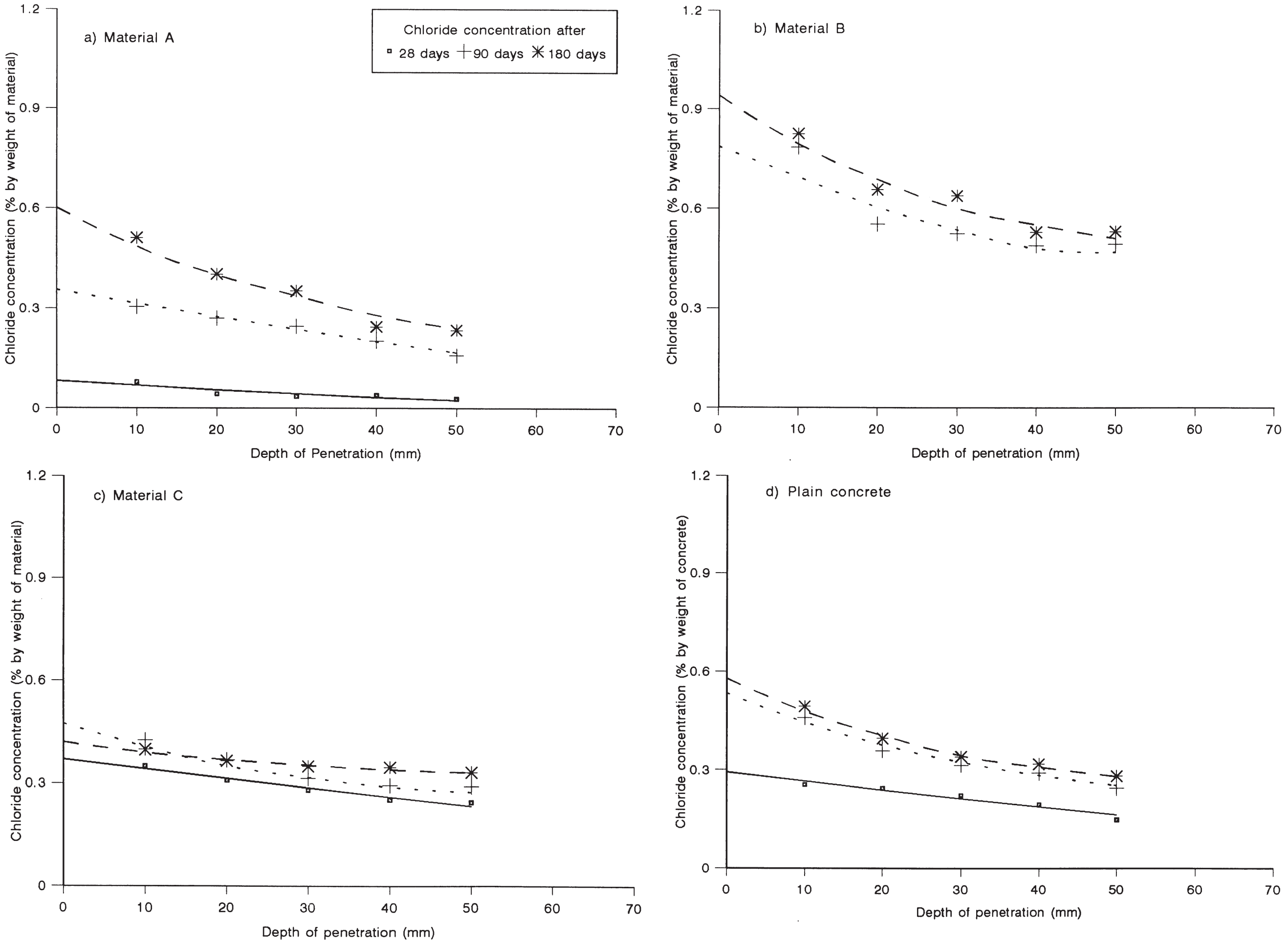

Fig. 5. Chloride diffusion profiles for (a) material A, (b) material B, (c) material C, and (d) concrete. Initial curing: water at 20°C for 28 days.

The regression analysis yielded the values of the coefficients C_0 and D_c for each material at different test ages. In addition it provided the best-fit profiles of the chloride concentration vs. depth of penetration relationships, which are plotted as curves in Fig. 4.

The profiles for repair materials A and B and concrete in Figs. 4(a), (b), and (d) show that chloride concentrations increase sharply at 90 days of exposure (relative to 28 days). Thereafter, the rate of increase slows down, leading to smaller increases at 180 days. The increase in chloride concentration with period of exposure is greatest near the surface of the repair materials and decreases sharply with depth. Beyond 30–40 mm depth, the increase in chloride concentration after 28 days exposure is insignificant.

The permeability coefficients of materials A, B, and C and concrete are 2.5×10^{-13}, 5.6×10^{-11}, 1.3×10^{-13}, and 1.1×10^{-12} m/sec, respectively (Table 1). These values show that the permeability of repair material B is up to two orders of magnitude higher than the other materials. The consequence of its higher permeability is the highest levels of chloride concentration in repair material B [Fig. 4(b)] compared to other materials [Figures 4(a), (c), and (d)]. However, the results also show that permeability is not the dominant factor that governs chloride penetration. For example materials A and C have similar permeability coefficients (2.5×10^{-13} and 1.3×10^{-13} m/sec, respectively) while the concrete is more permeable ($1.1 \times 10^{-12)}$, but the chloride diffusion profiles of material C [Fig. 4(c)] are radically different from materials A and concrete. The chloride diffusion profiles of material C are relatively flat, show small increase in chloride concentration from 28 to 180 days exposure, and the increase is similar at all depths. In contrast, the profiles for materials A and concrete are much steeper at depths from 0 to 30 mm, especially at 90 and 180 days exposure [Figures 4(a) and (d)]. The reason for the radically different chloride penetration characteristics of material C is its composition, which incorporates a styrene acrylic copolymer. The hardened material develops a continuous network of the polymer phase that attracts moisture into the material. The result is higher migration of Cl^- dissolved in the solution. The higher moisture attraction/retention capacity of the polymer phase is also verified by the fact that material C has by far the highest creep, shrinkage, and expansion (at 100% relative humidity) compared to the other materials [9].

The 90- and 180-day chloride concentration profiles of concrete [Fig. 4(d)] show much higher chloride concentrations near the surface than the other two materials A and C. In the surface zone, the chloride concentrations of concrete are, in fact, similar to the chloride concentrations in the highly permeable material B [Fig. 4(b)]. It is clear, therefore, that for the repair materials tested, a simple correlation between permeability and chloride penetration does not exist. This is due to the fact that different generic repair materials are comprised of chemically different constituents. For example, material A is based on Portland cement and contains admixtures that control shrinkage and expansion, material B is based on a non-Portland cement mineral binder that produces a porous repair, and material C incorporates a polymer latex that alters the moisture diffusion characteristics.

3.2.2. Initial curing: 28 days in water at 20°C

The chloride diffusion profiles of repair materials A, B, and C and concrete, which were cured in water at 20°C for 28 days prior to exposure to chloride environment, are plotted in Fig. 5. The best-fit curves representing Fick's second law of diffusion are plotted together with the average experimental data points. A comparison of these figures shows that the highest levels of chloride concentration occur in material B [Fig. 5(b)]. This is consistent with the observations made in the previous section and is due to the highest permeability of repair material B relative to the other materials.

A comparison of Figs. 4(a) and 5(a), both representing repair material A but with initial curing of 24 h and 28 days (at 20°C, 100% relative humidity) respectively, shows extremely low chloride concentrations at 28 days exposure to a chloride environment in Fig. 5(a). The increase in chloride concentration at 180 days exposure (relative to 28 days) is much more pronounced in Fig. 5(a), such that Figs. 4(a) and 5(a) show similar chloride concentrations with depth at 180 days exposure. A comparison of Figs. 4(b) and 5(b), representing repair material B, show that after 180 days of exposure to a chloride environment the chloride concentration profiles are fairly similar. The chloride concentrations are marginally higher at the surface of the 24-h (initially) cured

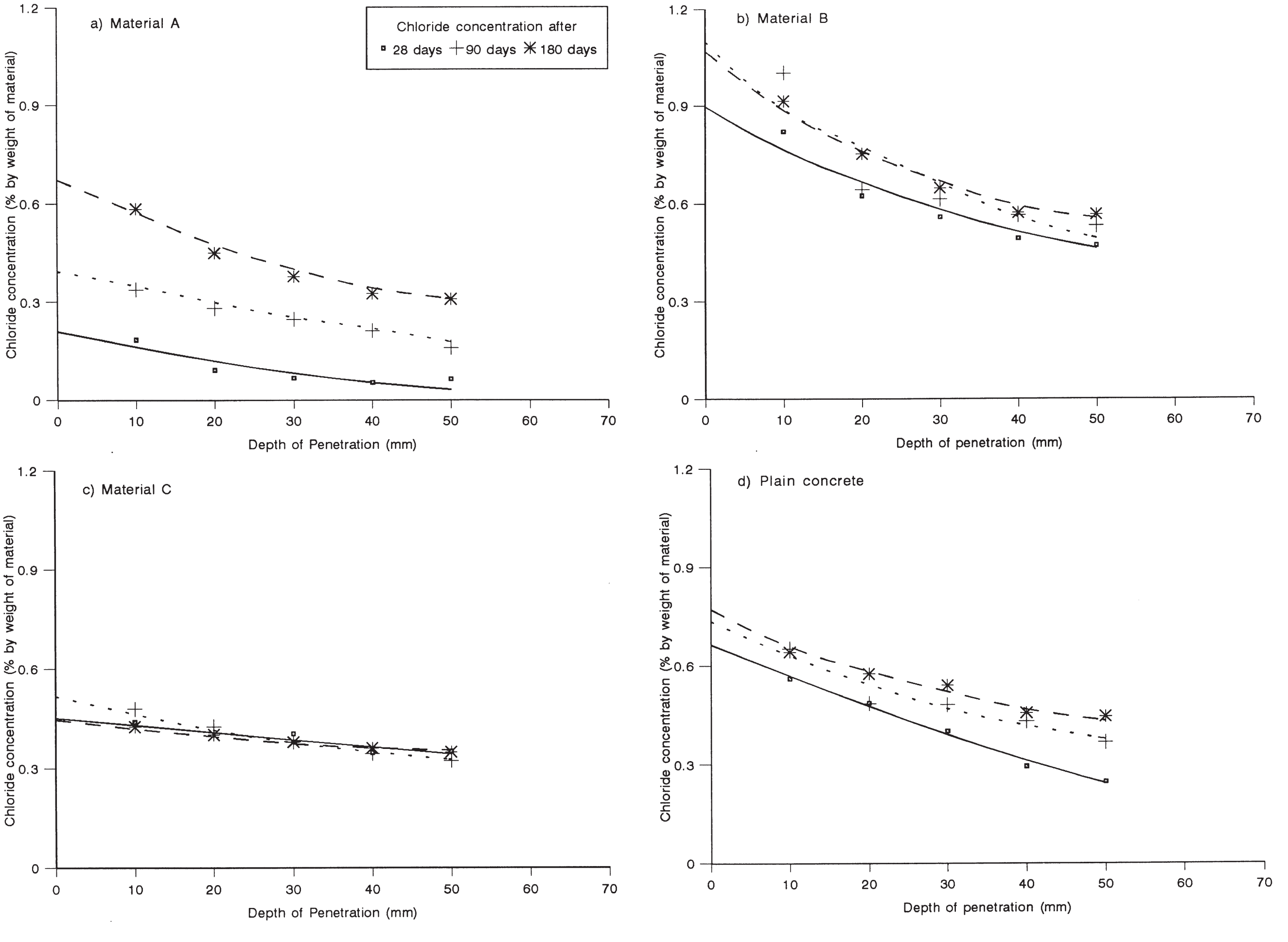

Fig. 6. Chloride diffusion profiles for (a) material A, (b) material B, (c) material C, and (d) concrete. Initial curing: air at 20°C, 55% relative humidity for 28 days.

material [Fig. 4(b)]. At higher depths, chloride concentrations are similar, with a value of about 0.6% at depths exceeding 30 mm from the surface. A comparison of Figs. 4(c) and 5(c) (for material C) confirms the very flat chloride concentration profiles with depth. In both figures, representing 24-h and 28-days (wet) initial curing respectively, the increase in chloride concentration from 28 to 180 days of exposure is small at all depths. In the case of 24-h initial curing [Fig. 4(c)], however, the chloride concentrations are somewhat higher in the surface zone compared with the 28-day initial wet curing case [Fig. 5(c)]. At depths greater than 20 mm, in the case of 180 days of exposure to a chloride environment, the chloride concentrations are similar for both initial curing conditions.

A comparison of the 180 days of exposure data in Figs. 4(d) and 5(d), representing concrete subjected to initial curing for 24 h and 28 days (wet) respectively, shows that limited initial curing (24 h) is more critical for concrete compared with the other repair materials A, B, and C considered above. For depths of 0 to 30 mm from the surface, the chloride concentrations are much greater in the concrete cured initially for 24 h relative to the 28-day (wet) cured material. At depths greater than 30 mm, chloride concentrations become similar at about 0.3% (by weight of concrete). These results indicate that adequate initial curing is necessary for concrete with reinforcement cover less than 30 mm.

3.3.3. Initial curing: 28 days at 20°C, 55% relative humidity

The chloride diffusion profiles of materials A, B, and C and concrete, which were initially air cured for 28 days (20°C, 55% relative humidity) are plotted in Figs. 6(a) to (d), respectively. The initial air curing is representative of common field conditions where idealised curing at very high humidity is not provided. A comparison of these figures with the chloride diffusion profiles of initially wet-cured repair materials [Figs. 5(a) to (d)] shows the relative effectiveness of repair materials to resist chloride penetration under dry conditions of curing. A comparison of Figs. 5(a) and 6(a) for repair material A shows that initial air curing results in marginally higher chloride concentration at all depths. Similar observations are repeated for material B when comparing Figs. 5(b) and 6(b). The chloride concentration profiles for material C are quite flat in both Figs. 5(c) and 6(c) and show slightly higher chloride concentrations at all depths under initial air curing. A comparison of Figs. 5(d) and 6(d) for concrete shows that the effect of initial air curing (relative to wet curing) is much more pronounced in concrete than in any of the repair materials A, B, and C. These results indicate that the repair material formulations investigated in this research are more effectively tailored (than concrete) to resist chloride penetration under practical curing conditions to which repair patches are exposed on site.

3.4. Relation between diffusion coefficient D_c and exposure period

The diffusion coefficients D_c and surface chloride concentrations C_0 were calculated by applying Fick's second law of diffusion to the experimental data plotted in Figs. 4 to 6 and carrying out a regression analysis to determine the best-fit curve. Typical relationships of D_c with exposure

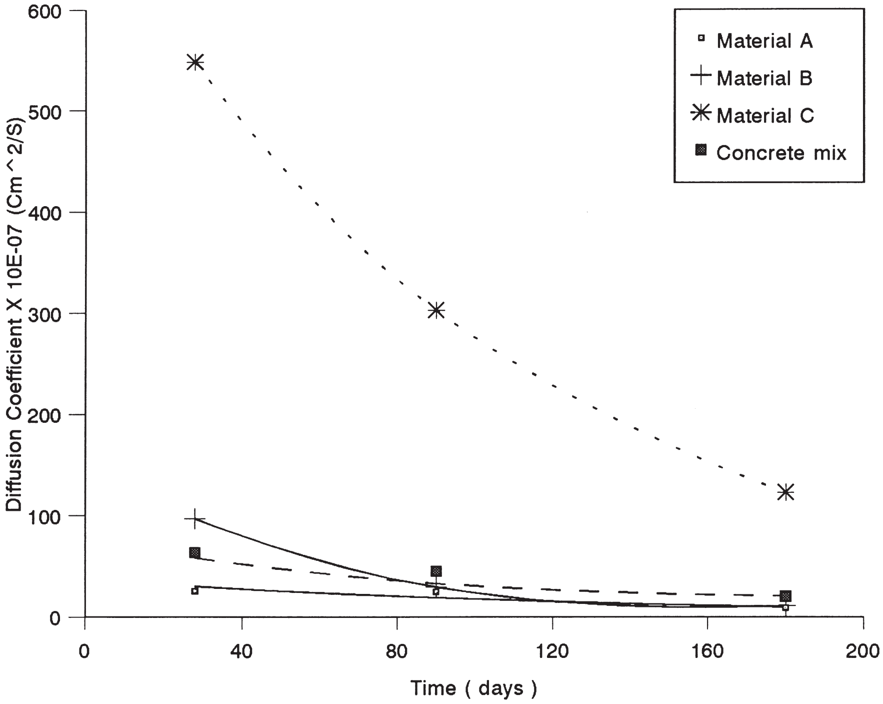

Fig. 7. Diffusion coefficient versus exposure time for repair materials A, B, and C and concrete. Initial curing: 28 days at 20°C, 55% relative humidity.

Table 2
Diffusion coefficients of repair materials subjected to different initial curing conditions

		Diffusion coefficient $D_c \times 10^{-7}$ (cm^2/s)		
Initial curing	Material	28 days	90 days	180 days
24 h in the mould	A	137.2	33.1	25.7
	B	518.6	234.80	84.9
	C	154.1	104.5	96.0
	Concrete	22.7	4.50	3.60
28 days in water at 20°C	A	46.4	31.0	15.4
	B	–	46.0	29.4
	C	309.0	107.3	94.4
	Concrete	152.9	21.7	17.2
28 days in air at 20°C, 55% relative humidity	A	25.5	24.8	9.2
	B	96.9	29.4	11.2
	C	548.2	302.8	123.0
	Concrete	63.4	55.2	20.3

time are plotted in Fig. 7 for the case of initial air curing for 28 days. Fig. 7 shows that values of D_c decrease nonlinearly with time. The diffusion coefficients D_c of all the repair materials for the different initial curing conditions are listed in Table 2 at exposure periods to a chloride environment of 28, 90, and 180 days. Each repair material for any given initial curing condition shows a reduction in D_c with time.

The range of D_c values for all the repair materials (including concrete) in Table 2, after 180 days exposure, is 3.6×10^{-7} to 123.0×10^{-7} cm^2/s. A comparison of these values with a wide range of data for marine concretes available in literature [7–9,14–17] shows that under long-term marine exposure (tidal zone and splash zone exposure up to 2000 cycles) the D_c values range between 0.2×10^{-7} and 2.2×10^{-7} cm^2/s. The marine concrete mixes represent low water/binder ratios and a variety of binders ranging from Portland cement to blended binders containing pulverized fuel ash (pfa), ground granulated blast furnace slag (bfs), microsilica, etc. The above comparison between repair materials and marine concretes shows that D_c values of repair materials are over an order of magnitude greater than the values for marine concretes. This is due to the high PC or blended cement content of the marine mixes ($>$430 kg/m^3), with low water/cement ratios compared with binder contents less than 350 kg/m^3 for the repair materials with higher water/cement ratios.

3.5. Relation between C_0 and exposure period

The values of C_0 are plotted against time for materials initially cured for 24 h (Fig. 8) and for 28 days initial curing in water at 20°C (Fig. 9). These figures generally indicate an increase in C_0 with increasing exposure period. Fig. 8 shows that for materials A and C and concrete the values of C_0 after 28 days chloride exposure range between 0.27 and 0.6% by weight of material. In comparison (Fig. 9), the corresponding range of C_0 for initially wet-cured specimens exposed for 28 days to a chloride environment is 0.07 to 0.4%. Clearly, C_0 values are higher for materials initially cured for 24 h compared with the specimens cured for 28 days.

After 180 days of exposure, C_0 values are between 0.6 and 0.85% (by weight of material) for specimens initially cured for 24 h in the mould (Fig. 8). The corresponding range for both the initial curing conditions of 28 days wet at 20°C (Fig. 9) and 28 days in air at 20°C, 55% relative hu-

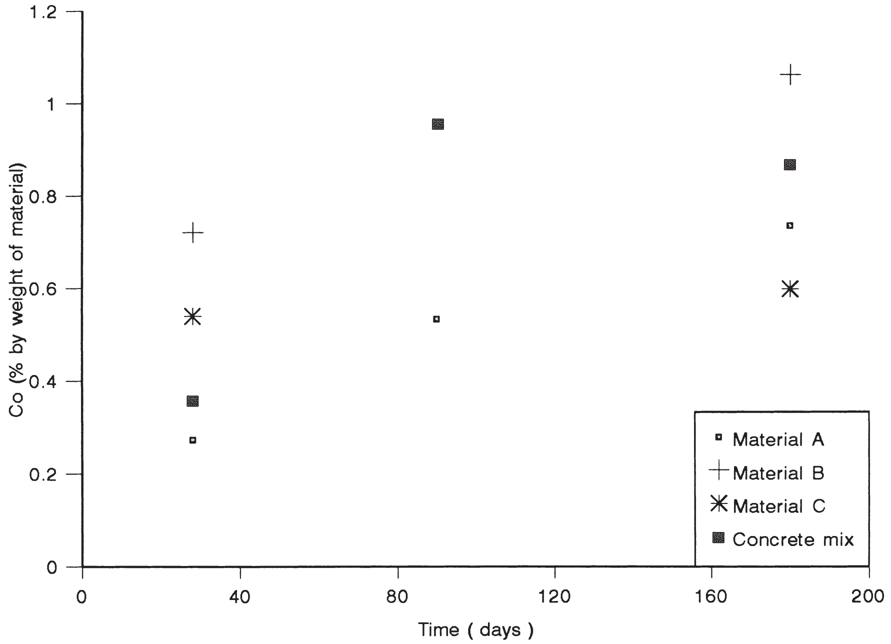

Fig. 8. Equilibrium chloride concentration C_0 with time for repair materials A, B, and C and concrete. Initial curing: 24 h in the mould after casting.

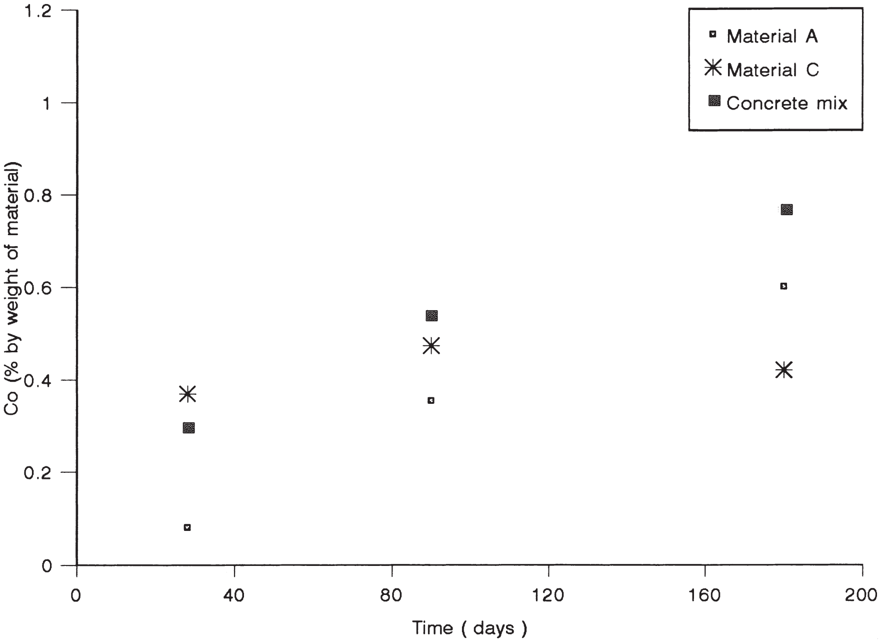

Fig. 9. Equilibrium chloride concentration C_0 with time for repair materials A, and C and concrete. Initial curing: in water at 20°C for 28 days.

midity is 0.4 to 0.8%. This suggests that in the long term the effect of initial curing on C_0 is small. The average value for C_0 for materials A and C and concrete at 180 days of exposure to a chloride environment can, therefore, be taken as 0.6 for all the three initial curing conditions investigated. The average value of C_0 for the highly permeable material B after 180 days of exposure for the three different initial curing conditions is taken as 1.0. These values of C_0 are used for long-term predictions of chloride penetration in the repair materials in the next section. The C_0 values for repair materials listed above fall within a comparable range obtained for marine concretes exposed to tidal cycles in the North Sea. Typical values ranged between 0.4 and 0.7% (by weight of concrete) over exposure periods in the tidal zone of up to 3 years [14]. C_0 values for marine concretes exposed to 1200 to 2000 seawater spray cycles in the laboratory ranged between 0.6 and 1.0% by weight of concrete [7,8].

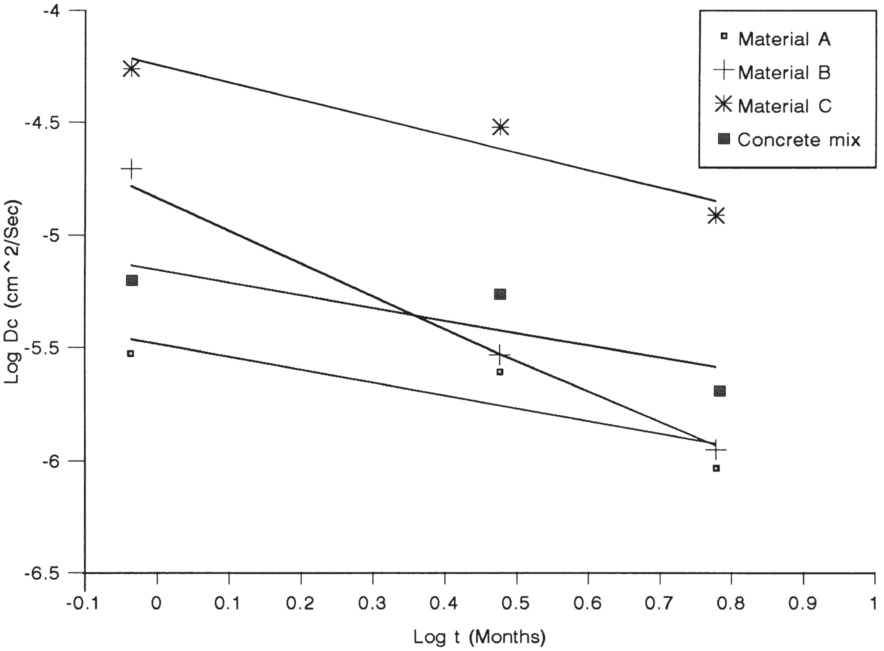

Fig. 10. Relation between D_c and time for repair materials A, B, and C and concrete. Initial curing: in air at 20°C, 55% relative humidity for 28 days.

Table 3
Values of D_i and m for materials A, B, and C and concrete under different initial curing

Material	Initial curing	m	D_i, cm^2/s
A	24 h in the mould	0.91	8.73
B		0.98	92.2
C		0.58	0.08
Concrete		0.92	1.67
A	28 days in water at 20°C	0.5	0.007
B		1.1	205.85
C		0.7	0.782
Concrete		0.6	0.076
A	28 days in air at 20°C, 55% relative humidity	0.57	0.011
B		1.41	10164.8
C		0.65	0.768
Concrete		0.52	0.013

3.6. Prediction of long-term chloride concentration

The experimental data for the effective diffusion coefficient D_c given in Table 2 and Fig. 7 show that the coefficient is time-dependent. The relationship between D_c and time can be approximated by an empirical relationship of the form shown in Eq. (3) [10]:

$$D_c = D_i t^{-m} \tag{3}$$

where D_i = effective diffusion coefficient at time t equal to 1 s and m = empirical constant. Eq. (3) can be written in a linear form as Eq. (4):

$$\log D_c = \log D_i - m \log t \tag{4}$$

To determine the values of D_i and m for the repair materials, the experimental data of D_c against t are plotted in the form of Eq. (4). A typical example of the resulting graph is shown in Fig. 10 for all materials initially cured in air for 28 days. The slope of the linear graphs in Fig. 10 gives the value of m and the intercept gives log D_i for each repair material. The resulting values of m and D_i determined from plots such as Fig. 10 for initial curing conditions of 24 h, 28 days wet at 20°C, and 28 days air at 20°C, 55% relative humidity are listed in Table 3. Both the D_i and m values for material B are high due to its excessive permeability. Hence, this material is not suitable for exposure in a chloride environment, but can be ideal for leaching chemicals from the substrates.

To predict long-term chloride concentrations in the repair materials, the time dependence of the diffusion coefficient D_c needs to be incorporated in Fick's second law of diffusion [13], which, in its general form, is given by the differential Eq. (5):

$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 c}{\partial x^2} \tag{5}$$

Substituting the time variable expression for D_c [Eq. (3)] into Eq. (5) gives Eq. (6):

$$\frac{\partial C}{\partial t} = D_i t^{-m} \frac{\partial^2 c}{\partial x^2} \tag{6}$$

A standard solution for Eq. (6) gives Eq. (7) [14]:

$$C_{(x,t)} = C_0 \left[1 - erf \left(\frac{x}{2\sqrt{\frac{D_i}{(1-m)} t^{(1-m)}}} \right) \right] \tag{7}$$

Eq. (7) can be used to predict long-term chloride concentrations in the repair materials by substituting the values of D_i, m (Table 3), and C_0, which have been determined experimentally.

In order to make an assessment of the relative performance of the repair materials in the long term, chloride concentrations at a cover depth of 30 mm have been calculated using Eq. (7) after 10 years of exposure to a chloride environment. The three initial curing conditions of (a) 24 h after casting, (b) water curing at 20°C, for 28 days, and (c) air curing for 28 days at 20°C, 55% relative humidity are considered. The values of D_i and m listed in Table 3 have been

Table 4
Predicted chloride concentrations after 10 years of exposure to a chloride environment

Material	Initial curing	Average C_0 (%)*	Chloride concentration after 10 years (%)**
A	24 h in the mould	0.6	0.558
B		1.0	0.978
C		0.6	0.560
Concrete		0.6	0.499
A	28 days in water at 20°C	0.6	0.536
B		1.0	–
C		0.6	0.274
Concrete		0.6	0.132
A	28 days in air at 20°, 55% relative humidity	0.6	0.509
B		1.0	–
C		0.6	0.384
Concrete		0.6	0.430

* Long-term value represented by the 180 days data.

** Predicted using Eq. (7) at 30-mm cover to reinforcement.

Table 5
Chloride concentration after 10 years of exposure

	Initial Curing		
Material	28 days wet, 20°C (%)	24 h in mould (%)	28 days at 20°C, 55% relative humidity (%)
Concrete	0.132	0.499	0.430
Repair material A	0.536	0.558	0.509

used to calculate the chloride concentrations. The average long-term values of C_0 (at 180 days) were substituted for each material and initial curing condition. The resulting chloride concentrations are listed in Table 4.

The predicted chloride concentrations in Table 4 show that inadequate wet curing before exposure to the chloride environment is much more critical for concrete than for repair materials A or C. Repair material A has fairly similar chloride concentrations of over 0.5% for all the three initial curing conditions. The concrete mix has very low chloride concentration of 0.132% when initially cured in water, whereas both the 24-h curing and the initially dry curing (28 days) result in chloride concentrations in excess of 0.4%.

4. Conclusions

The following conclusions are based on the test results reported in this paper.

1. A simple correlation between permeability and chloride penetration does not exist for the different repair materials and control concrete. This is because different generic repair materials are comprised of chemically different constituents, such as polymers and admixtures, which control shrinkage and other conditions.
2. Repair materials that incorporate a polymer admixture show a much lower rate of reduction in chloride concentration with increasing depth from the surface relative to concrete and other generic types of repair materials.
3. Inadequate wet curing before exposure to a chloride environment is much more critical for concrete than for commercially formulated repair materials. For example, it has been estimated that at a cover of 30 mm the chloride concentration after 10 years exposure to a chloride environment for a concrete mix and a high strength (and low permeability) repair material will be the values shown in Table 5.
4. The long-term chloride penetration in repair materials can be predicted from a modified equation based on Fick's law of diffusion, which takes account of the variation of diffusion coefficient D_c with time.
5. The range of D_c values for the different repair materials is 3.6×10^{-7} to 123.0×10^{-7} cm^2/s. In comparison the D_c values of marine concretes range between 0.2×10^{-7} and 2.2×10^{-7} cm^2/s.

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