

Effectiveness of surface coatings to protect reinforced concrete in marine environments

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Paper received: January 21, 2000; Paper accepted: April 6, 2000

ABSTRACT

Coatings can contribute to extending service life of concrete structures exposed to marine environments by reducing the rate of chloride penetration. In the present paper, the effect of coatings on the rate of chloride uptake was studied by measuring their concentration profiles at different times, extending up to 24 months. Using a solution of the so-called Fick's second law of diffusion, least-square fitting leads to the value of chloride concentration under the coating (C_o) which allowed us to compare the effectiveness of different coatings. Depending on the formulation, some of the studied acrylic coatings could reduce the value of C_o by more than 80% in comparison to the unpainted concrete. Water permeability coefficients were measured for the same coatings, according to EN 1062-3. The ranking of effectiveness to stop chlorides is the same as the water imperviousness, but the minimum requirement proposed by prEN 1504-2 ($0.1 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-0.5}$) did not prove to be enough for an efficient protection against chloride permeation.

RÉSUMÉ

Les revêtements peuvent contribuer à l'extension de la durée de vie des structures en béton exposées à des environnements marins en réduisant le taux de pénétration des chlorures. Dans cet article, l'effet des revêtements sur le taux de pénétration des chlorures dans le béton a été suivi en mesurant leurs profils de concentration à des périodes différentes, jusqu'à 24 mois d'exposition. En utilisant une solution de la seconde Loi de Fick, nous avons appliqué la méthode des moindres carrés au taux de concentration en ions chlorures sous le revêtement (C_o), afin de comparer l'efficacité de plusieurs revêtements. Selon la formulation, quelques peintures acryliques qui ont été étudiées ont pu réduire la valeur de C_o de plus de 80% en comparaison avec le béton sans revêtement. Les coefficients de perméabilité à l'eau des mêmes revêtements ont été obtenus d'après la norme européenne EN 1062-3. Le classement des revêtements par degré d'efficacité contre l'entrée des chlorures est le même que pour leur imperméabilité à l'eau, mais la quantité minimale mentionnée dans le projet de norme européenne EN 1504-2 ($0,1 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-0.5}$) n'est pas suffisante pour que le revêtement protège de façon efficace le béton contre la pénétration des chlorures.

1. INTRODUCTION

Concrete can be a highly durable construction material as long as care and quality control are enforced at all stages of the design, production and construction processes. However, experience has demonstrated that its potential long-term durability is not always achieved, leading to early failure of reinforced concrete structures.

It is now accepted that the durability of the reinforced concrete depends mainly on the composition and properties of the concrete surface layer [1]. This layer, sometimes with a thickness close to the cover of the reinforcement, is the only responsible for the corrosion protection of the reinforcement.

Steel reinforcement in concrete remains protected against corrosion as long as it stays passive. The two processes reported to be mainly responsible for depassivation and corrosion of embedded steel bars are:

- the pH reduction in concrete, caused by the action of carbon dioxide (carbonation)
- chloride ions ingress into concrete

Either CO_2 or chlorides can lead to the steel depassivation as soon as the carbonation front reaches the rebars or the chloride concentration around them attains a critical value.

However, water is the most critical agent because it lies on the root of many important degradation processes: it is related with freeze-thaw durability, pro-

Editorial Note

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vides the transport path for chloride ions and establishes electrolytic continuity inside concrete. Besides, in order that the carbonation reaction takes place the presence of a certain amount of water is required, albeit within bounds - the maximum carbonation rate is reached between 40-80% relative humidity [2, 3].

One way to avoid the action of the aforementioned aggressive agents consists in cutting off their transportation path into concrete. Surface coatings with appropriate "barrier" characteristics can do this job and in marine environments they should prevent or at least delay the penetration of chlorides into concrete.

The pre-standard prEN 1504-2 [4] establishes as a minimum requirement for coatings for concrete ingress protection that the water permeability coefficient should not exceed $0.1 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-0.5}$. It is an open question whether this value also guarantees enough chloride penetration resistance for practical uses.

This work intends to contribute to a better understanding of this issue, by presenting data of chloride intake and water permeability of several coatings used for protecting concrete.

2. OVERVIEW OF COATING MATERIALS SPECIFICATIONS

The availability of a wide range of coatings rises problems in their choice since they can provide different levels of protection while presenting different characteristics among similar generic chemical composition [5]. This means that their "barrier" properties and their effect on concrete must be evaluated.

In recent years, several test methods as well as some requirements have been issued as drafts standards for CEN public enquiry. Those related with coatings for concrete protection are [4, 6]:

- prEN 1504-2, 2000 - Surface protection systems
- ENV 1504-9, 1997 - General principles for the use of products and systems.

The aforementioned EN standards will help the selection of products to be used in new or repaired structures as long as the intended use or main function required from the protection system is defined and the type of exposure is known.

According to those standards, coatings can be used as a protection and repair "method" of concrete structures, making use of one or more of the following five basic "principles" which are based on the chemical or physical laws allowing the prevention or stabilisation of the chemical and physical deterioration processes in the concrete or the electrochemical corrosion processes on the steel surface:

- ingress protection
- moisture control
- physical resistance
- resistance to chemicals
- increasing resistivity.

For each of those five "principles" two groups of performance characteristics could be evaluated on the

coating system:

- characteristics for all intended uses
- characteristics for certain intended uses.

These characteristics are already defined in prEN 1504-2 as well as almost all of the requirement values an overview of which is presented in Table 1. As can be seen, adhesion (pull-off test or cross cut performance) is a compulsory specification for all intended uses and the other mandatory characteristics for coatings used for ingress protection are: permeability to CO_2 , permeability to water vapour and capillary absorption and permeability to liquid water.

Standardised laboratory tests as those indicated on Table 1 make it possible to obtain objective data to assess the potential properties of the products under a comparative basis. Nevertheless, in order to be useful, the laboratory results must agree with the performance of the products under field conditions. However, few published data are available on parallel evaluation of products either in laboratory or in field allowing a validation of the laboratory results. The aim of the methodology adopted for the present study is to validate the laboratory tests by comparing their results with those obtained in the field.

3. EXPERIMENTAL PROTOCOL

The studied coatings, representing typical examples of products used in construction, are acrylic based and form films by solvent evaporation. They were applied on the substrate by brush following the recommendations of the manufacturers, as given in Table 2.

3.1 Laboratory testing

The purpose of the tests performed in laboratory was the evaluation of the "barrier" properties of the paint films against chlorides by determining their permeability to sodium chloride.

Because chlorides are transported in water phase, the coatings capillary absorption/permeability to water was also evaluated. The corresponding results are related to parallel laboratory and field measurements of the resistance of the coatings to chloride intake.

3.1.1 Resistance to ingress of water

The resistance to water intake was evaluated by determining the coating "capillary absorption/permeability" to water. A gravimetric method was used, following the prEN 1062-3 (see Table 1), in order to obtain the water permeability coefficient, w . To evaluate the influence of the substrate in this parameter, the coatings were applied over two types of substrates - clay bricks and concrete made with a mix proportion of 1: 4.18: 3.38: 0.70 (cement Portland: sand: coarse aggregate: w/c ratio).

3.1.2 Resistance to chloride ingress

The resistance to chloride ingress was evaluated by determination of the mass transport coefficient of sodium

Table 1 - Performance characteristics for coatings according to pr EN 1504-2

Performance characteristics	Test method protection	Principles				
		Ingress control	Moisture resistance	Phys. resistance	Chem. resistivity	Increas.
Linear shrinkage	prEN 12617-1	□	□	□	□	□
Compressive strength	prEN 12190			■	□	
Coeff. thermal expansion	EN 1770	□	□	□	□	□
Abrasion resistance	ISO 7784-2			■		
Adhesion by cross cut ^(a)	EN ISO 2409	□	□	□	□	□
Permeability to CO ₂	prEN 1062-6	■				
Permeability to water vapour	prEN 1062-2	■	■			■
Capillary absorption and permeability to water	prEN 1062-3	■	■			■
Diffusion of chloride ions ^(b)	104-838	□				
Adhes. after thermal compatib.						
• Freeze-thaw cycl. (salt immers.)	13687-1	□	□	□	□	□
• Thunder shower cycl.	13687-2	□	□	□	□	□
• Thermal cycl. (no salt impact)	13687-3	□	□	□	□	□
Resist. to thermal shock	13687-5	□		□	□	
Chemical resistance	ISO 2812-1	□				
Resist. to high chemical attack	prEN 13529				■	□
Crack bridging ability	prEN 1062-7	□	□	□	□	□
Impact resistance	ISO 6272			■		□
Adhesion by pull-off test	EN 1542	■	■	■	■	■
Fire resist. after application	(TC 127)	□	□	□	□	□
Skid resistance	(TC 227)	□	□	□	□	□
Artificial weathering	prEN 1062-11	□	□	□	□	□
Antistatic behaviour	EN 1081	□	□	□	□	
Physiological performance	(national regulations)	□	□	□	□	□
Adhesion on wet concrete	pr EN 13578	□	□	□	□	

■ for all intended uses; □ for certain uses

(a) Mandatory for thin layers (up to 0.5 mm) where pull-off not possible;

(b) No requirement is defined yet

chloride in the paint films, *L*. The test method and the theoretical background in which the calculation of *L* was based are fully described in [7] and summarised below.

Experimental set-up

A permeation cell method was used in which the permeation cell was made up of two half-cells sealing the specimen between them. One half of the cell contained deionised water and the other half an aqueous 2.5 M sodium chloride solution. The experimental arrangements under which the permeability to the salt was studied are represented in Fig. 1.

The coatings were applied on a porous substrate, in this case unglazed ceramic plates 4.74 cm thick, and dried during at least one month. Meanwhile, circular discs were cut from the coated plates and the thickness of

the coating film in an area adjacent to the permeation area was measured according to ISO 2808 "Paints and varnishes - Determination of film thickness" - Method 5B - "Measurement of dry film thickness: microscope methods".

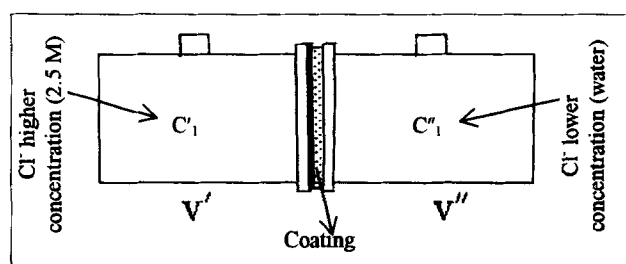


Fig. 1 - Permeation cell.

Product	Binder type	Film type and texture	Solvent/dispersant	Solids content) (% v/v)	Application (3 coats)		
					Coverage rate, m ² /l (each coat)	Dilution, % v/v	Approx. dry thickness, μm
A	Poly(acrylate)	Pigmented/smooth	Water	39	10	1st: 10%; 2nd/3rd: 5%	120
B	Poly(acrylate) modified with vinyltoluene	Pigmented/smooth	Org.solvent	45	8	None	160
C	Poly(acrylate)	Pigmented/textured	Water	50	7	1st: 20%; 2nd/3rd: none	225
D	Poly(methacrylate)	Unpigmented	Org.solvent	29	7	None	100
E	Poly(methacrylate)	Pigmented/smooth	Org.solvent	46	8	None	180
H	Poly(methacrylate)	Pigmented/smooth	Org.solvent	1stcoat: 34 2nd/3rd: 36	7 8	1st: 15%; 2nd/3rd: 5%	110
I	Poly(methacrylate)	Pigmented/textured	Org.solvent	1stcoat: 34 2ndcoat: 36 3rdcoat: 59	7 8 3	1st: 15%; 2nd: 5%; 3rd: 10%	230
S	Poly(acrylate)	Pigmented/smooth	Water	45	7	1st: 5%; 2nd/3rd: none	180

Theoretical background

Considering that the porous support does not substantially interfere in the mass transport mechanism inside the film, a mass transport coefficient can be calculated that is related with the coating permeability to chloride ions. That coefficient was obtained from the Nernst-Planck Equation (1) applied to the case of electrolyte diffusion across a membrane. This equation expresses the flux of the *i*th ion, N_i , inside that membrane as the sum of three terms representing convection, diffusion and migration due to electrostatic potential gradients [8-10]:

$$-N_i = -c_i u + D_i \left(\frac{dc_i}{dz} + z_i c_i \frac{F}{RT} \frac{d\Psi}{dz} \right) \quad (1)$$

where,

c_i – concentration of species or component *i* in the membrane phase, mol.m⁻³

u – mole average bulk velocity, m.s⁻¹

D_i – diffusion coefficient of species or component *i* within the membrane relative to membrane-fixed reference system, m².s⁻¹

z_i – valence of ion *i*

F – Faraday constant, 96 500 C.mol⁻¹

R – gas constant, 8.314 J.mol⁻¹.K⁻¹

T – absolute temperature, K

Ψ – electric potential in the membrane, V

In order to use Equation (1) for the mass transport coefficient calculation of a specimen across the coating, the following assumptions were made:

- Paint films can be classified as dense membranes in which the transport of small molecules occurs by a sorption-diffusion mechanism. This assumption has been accepted by several researchers for the case of the transport of water through coatings [11-13]. It is valid if the

pigmentation level in the paint film is below the CPVC (critical pigment volume concentration), otherwise the paint film becomes porous;

- The ion-exchange capacity of paint films is negligible. So, in the case of the transport of an electrolyte 1-1, anionic and cationic flows inside the film can be considered identical ($N_1 = N_2$) and anion concentration in the membrane phase is equal to cation concentration ($c_1 = c_2$);

- The substrate does not greatly affect the membrane properties of the coating film;

- The overall flux from the lower to the higher Cl⁻ concentration cell side, due to the osmotic pressure gradient, is negligible; this assumption can be accepted for the case of the less water permeable coatings, which are used in the concrete protection against chlorides and allows the simplification of Equation (1) in making $u = 0$.

Applying the above simplifications to Equation (1) and considering that the ions being transported are monovalent ions, Equation (2) is obtained [8] for the flux of anion 1 inside the membrane:

$$-N_1 = \bar{D} \frac{dc_1}{dz} \quad (2)$$

where \bar{D} is an average diffusion coefficient between diffusion coefficients of the anion 1 and cation 2, given by:

$$\bar{D} = \frac{2D_1D_2}{D_1 + D_2} \quad (3)$$

The kinetic Equation (2) and the mass balance across the membrane of thickness *l*, assuming that a pseudo-steady state regimen, yields the flux of anion 1:

$$N_1 = \frac{\bar{D}\bar{H}}{l} (C_1' - C_1'') \quad (4)$$

where,

C_1' – concentration of anion 1 in the solution at the

higher concentration cell side
 C''_1 – concentration of anion 1 in the solution at the lower concentration cell side.

\bar{H} is an average partition coefficient at the membrane interfaces that has a contribution of the partition coefficients of both ions in presence – H_1 (anion) and H_2 (cation). In the case of an electrolyte 1-1 in which cation and anion concentrations are equal, \bar{H} is given by the following expression [8]:

$$\bar{H} = \sqrt{H_1 \cdot H_2} \quad (5)$$

An overall mass balance on the adjacent compartments of the cell yields the expression:

$$-N_1 = \frac{V'}{A} \frac{dC'_1}{dt} = -\frac{V''}{A} \frac{dC''_1}{dt} \quad (6)$$

where A is the permeation area and V' and V'' are the solution volumes in the cell compartments.

Assuming a pseudo-steady state regimen inside the membrane, we may combine Equation (6) with the flux Equation (4), resulting in:

$$\frac{d}{dt}(C'_1 - C''_1) = \frac{\bar{D}\bar{H}A}{l} \left(\frac{1}{V'} + \frac{1}{V''} \right) (C''_1 - C'_1) \quad (7)$$

This differential equation is subject to the initial condition,

$$t = 0, \quad C'_1 - C''_1 = C'_{1(t=0)} - C''_{1(t=0)}$$

resulting in the following integrated solution:

$$\ln(C'_1 - C''_1) = -\frac{\bar{D}\bar{H}A}{l} \left(\frac{1}{V'} + \frac{1}{V''} \right) t + \ln(C'_{1(t=0)} - C''_{1(t=0)}) \quad (8)$$

The product $\bar{D}\bar{H}$ can be considered as an effective mass transport coefficient L , in this case with the same dimensions as a diffusion coefficient ($m^2 \cdot s^{-1}$). However this parameter is intrinsically different from a diffusion coefficient and can be more correctly considered as a “permeability coefficient” of the salt sodium chloride, because it has contributions from partition and diffusion coefficients of both ions being transported (Na^+ and Cl^-).

The product $\bar{D}\bar{H} = L$ was obtained by linear regression from the graphic representation of $\ln(C'_1 - C''_1)$ versus t , after the equilibrium of the permeation process has been reached. C''_1 was periodically measured using an ion selective electrode and the corresponding C'_1 was obtained by calculation.

In the present case the paint film was applied over a substrate and consequently the mass transport coefficient obtained from Equation (8) is referred to the whole (coating film+substrate), L_{C+S} . The coefficient for the coating film alone, L_C , was calculated using the following Equation [14]:

$$L_C = l_C \frac{1}{\frac{l_{C+S}}{L_{C+S}} - \frac{l_S}{L_S}} \quad (9)$$

where,

l_C – coating thickness, m

l_S – substrate thickness, m

l_{C+S} – (coating+substrate) thickness, m

L_S – mass transport coefficient correspondent to substrate alone, $m^2 \cdot s^{-1}$.

3.2 Field testing

In field, the effect of the coatings on preventing the chloride penetration into concrete was assessed using a methodology similar to that described in the document 104-838 (see Table 1) under discussion by CEN. According to this methodology, the chloride coating barrier effect is assessed by submitting painted and unpainted concrete slabs to an environment containing chlorides and measuring the chloride content at several layers inside the concrete, after a certain exposure period.

The ultimate goal of the exposure program was to calculate the apparent chloride diffusion coefficient, D^a , of painted and unpainted concrete at various ages and to evaluate the effect of the coatings on the value of this coefficient.

The experimental set-up and the theoretical background on which the calculation of D^a was based are described below.

Experimental set-up

The coatings were applied on one face of concrete slabs $8 \times 8 \times 4 \text{ cm}^3$. The concrete mix proportion was that already above-cited (see section 3.1.1). To expose only the painted test face to the source of chlorides, the other faces of the slabs were isolated from the atmosphere by a thick coating of epoxy resin, impermeable to water and CO_2 .

Painted and unpainted concrete slabs were exposed at Leixões sea harbour (Porto, Portugal) and, after different periods of exposure, some slabs were taken for chloride analysis at several depths (acid soluble “total” chloride content) and chloride profiles determination.

Theoretical background

The main chloride ions transport mechanisms in concrete are [15]:

- diffusion in result of chloride concentration gradients in the aqueous solution inside the concrete pores;
- capillary suction involving the transport of chlorides dissolved in water through the open pore system of the concrete;
- pressure driven convection resulting in the transport of chlorides dissolved in water.

All three transport mechanisms may occur simultaneously but in a practical situation, a simplified approach is commonly used assuming that only one mechanism dominates. When the pore system is unsaturated, capillary absorption may dominate. When the pore system is water saturated, a flow of fluid may occur if a sufficiently high-pressure head exists but, at normal pressure, the transport of ions by diffusion dominates.

The predominance of one of the referred transport mechanisms depends on the hygroscopic state of the material, on its pore structure and on the action of pressure gradients.

In a practical situation of concrete structures exposed to the atmosphere, the analysis of chloride uptake is commonly made by considering that the dominating mechanism is diffusional and the characterisation of the concrete with respect to its resistance to the permeation of chlorides is made by introducing an apparent coefficient, D^a . This coefficient is calculated by using the following equation of chloride mass conservation law:

$$J_{Cl} = \frac{\partial C_z}{\partial t} = \frac{\partial}{\partial z} \left(D^a \frac{\partial C(z)}{\partial z} \right) \quad (10)$$

where,

J_{Cl} – ion flux through a unit area per unit of time
 $C(z)$ – chloride concentration at a distance z from the exposed surface, after the period t of exposure to chlorides
 t – exposure time
 z – distance from surface (depth).

Equation (10) is the so-called Fick's 2nd law of diffusion and is usually solved assuming the following initial and boundary conditions,

$C(z) = 0, t = 0$; and $C(z) = C_0, z = 0$
 and the following postulations,

- Semi-infinite medium
- Apparent diffusion coefficient, D^a , constant in space and time
- Boundary condition C_0 constant for $t > 0$.

The solution [8, 14, 16] given by Equation (11) was used in laboratory and field tests by several researchers [17-21] to describe the penetration of chlorides into concrete:

$$\frac{C(z)}{C_0} = 1 - \operatorname{erf} \frac{z}{2\sqrt{D^a \cdot t}} \quad (11)$$

As the concrete slabs used in this work were 4 cm thick (l) and could not be considered a semi-infinite medium due to the fast advance of the chloride front during the exposure period analysed, Equation (11) was not applicable. Different initial and boundary conditions should be considered for the integration of Equation (10). These conditions are the following, having in mind that only the painted face of the slabs was exposed to the environment and all the others were isolated with the impermeable epoxy coating:

$C(z) = C_0, z = 0$; $C(z) = 0, t = 0$;
 $\partial C(z)/\partial z = 0, z = l$

The new solution of Equation (11) is [14]:

$$\frac{C(z)}{C_0} = 1 + \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{2n-1} \exp \left[-\frac{(2n-1)^2 \pi^2 t D^a}{4t^2} \right] \cos \left[\frac{(2n-1)\pi(l-z)}{2l} \right] \quad (12)$$

The above assumptions are not valid for real concrete structures because neither D^a nor C_0 are constant [18, 19, 22, 23]. In fact, any changes in temperature and relative humidity affect D^a . Besides, this latter coefficient tends to decrease with time due to continued cement hydration. Moreover, except for continuous immersion of concrete in a constant concentration salt solution, C_0 depends on the season of the year and, even

along the day, is not constant. However, for comparative experiments using the same concrete substrate painted with different coatings and exposed to the same conditions – as in this work – these assumptions could be adopted and Equation (12) was used.

An iterative method was used to find the values for C_0 and D^a by a least-squares fitting, using Equation (12) and $C(z)$ experimental data measured at various ages with different samples of painted and unpainted concrete.

4. RESULTS

4.1 Laboratory tests

Table 3 shows the water permeability coefficients of the coatings on each of the two substrates as well as the values for the two lone substrates. Some of the values are below the applicable limit of the test method pr EN 1062-3 (0.05 kg.m⁻².h^{-0.5}). However, they are presented for comparative purposes of the performance of the different coatings in order to discuss the maximum value proposed by CEN for coatings to protect concrete against the ingress of chlorides (0.1 kg.m⁻².h^{-0.5}).

As we can see from the results of Table 3, the influence of the permeability properties of the substrate on

Table 3 – Water permeability coefficients (pr EN 1062-3)

Specimen	w (kg.m ⁻² .h ^{-0.5})	
	On concrete	On clay brick
A	0.065	0.18
B	0.052	0.011
C	0.033	0.19
D	0.005	0
E	0.006	0.0011
H	0.007	0.0021
I	0.015	-
S	-	0.0091
Substrate	0.25	6.1

Table 4 – Mass transport coefficients according to Equations (8) and (9)

Specimen	Average film thickness, μm	$L_{C+S} \times 10^{13}$ [m ² .s ⁻¹]	$L_C \times 10^{14}$ [m ² .s ⁻¹]	Reduction factor
Ceramic plate	-	7.14×10^2	-	-
A	90	343	125	2.1
B	160	184	79.4	3.9
C	200	402	411	1.8
D	95	2.28×10^{-2}	4.5×10^{-3}	3.1×10^4
E	200	3.68	1.52	1.9×10^2
H	118	12.0	2.86	60
I	200	21.3	10.7	34
S	185	52.0	21.0	14

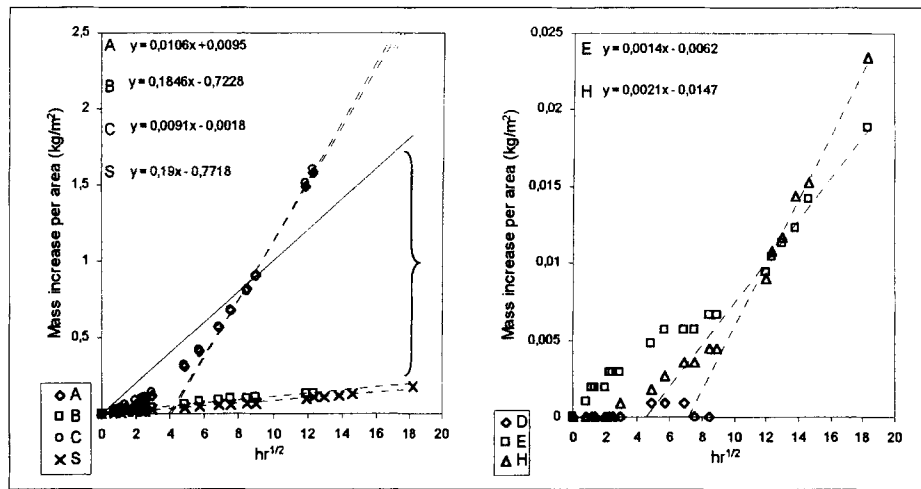


Fig. 2 – Assessment of the water permeability of the coatings applied on clay bricks.

the value of w is more pronounced for the more permeable coatings. The general ranking of the coatings effectiveness against permeation of water, evaluated from the values of w presented on last column of Table 3 is:
 $D > E > H > S > B > A > C$

It is worth mentioning that coating D (methacrylate solvent based varnish) was impermeable to water when applied over clay brick and the next less permeable coatings E and H reached the permeation equilibrium only after 3,5 days of testing. The most permeable coatings like A and C reached the permeation equilibrium faster, after 2 days of testing.

These two coatings are the only ones not fulfilling the requirement of pr EN 1504-2 ($w < 0.1 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-0.5}$). The performance of the different coatings is more clearly observed in Fig. 2.

Table 4 gives the mass transport coefficients of sodium chloride on the painted ceramic plates (L_{C+S}) and also those calculated by Equation (9) for the lone coatings (L_C). The presented results are average values from three test runs.

By inspection of the data in Table 4, it can be observed that all paints are effective in reducing the the permeation of the salt from about 2 to up to 10^4 times. However, the improvement due to the water-based acrylics (A, C and S) was much lower than that due to some of the solvent-based methacrylics (D, E and H). The overall ranking of effectiveness of the coatings against permeation of chlorides, evaluated from the reduction factor given in Table 4 is:
 $D > E > H > I > S > B > A > C$

It can be noticed that the ranking of the coatings against permeation of chlorides and water is the same.

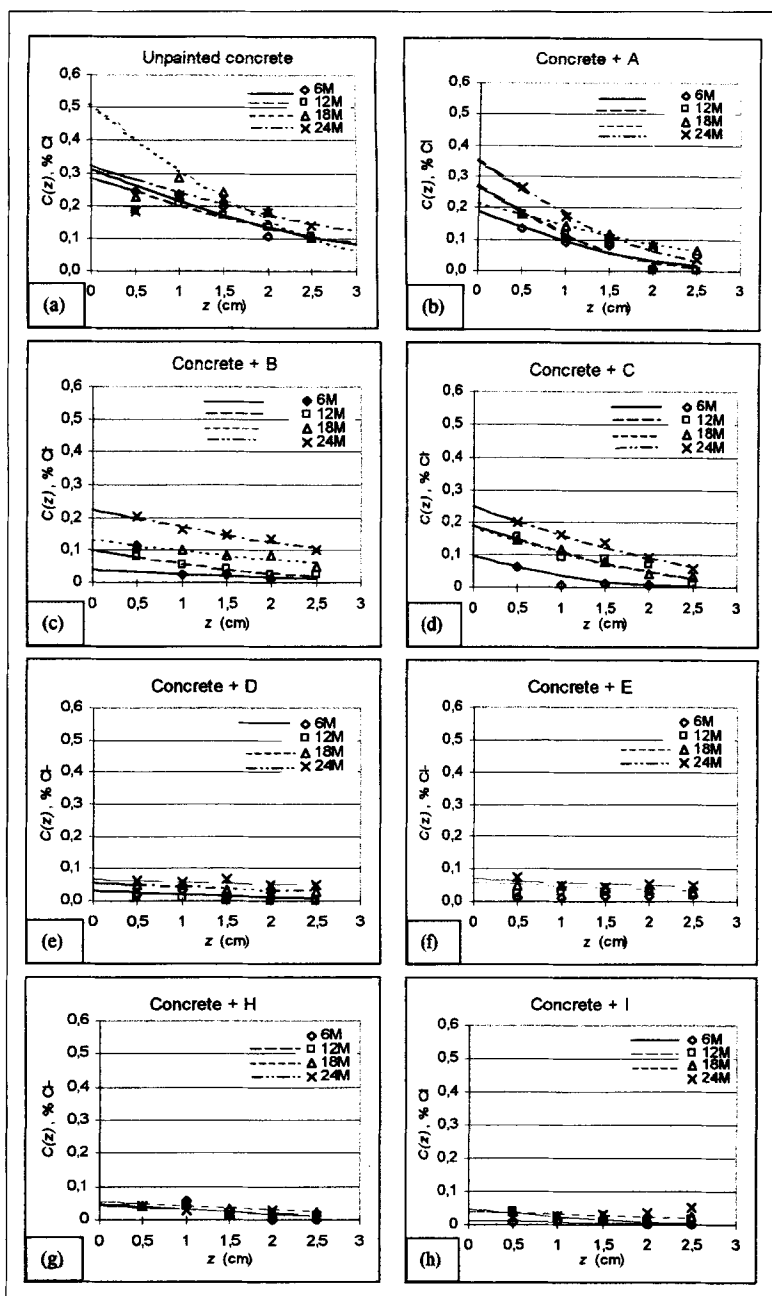


Fig. 3 – Chloride distribution in painted and unpainted concrete slabs exposed at Leixões harbour with fitted curves according to Equation (12).

4.2 Field tests

The data obtained for chloride content as a function of depth into concrete were used to find, by a least-square fitting (Equation (12)), the best fit values for the diffusion coefficient D^a and the apparent surface chloride concentration C_0 . These two parameters, presented in Table 5, were used to draw the curves presented in Fig. 3 (a-h). The evolution of the chloride profiles inside the painted and unpainted con-

Table 5 - Values of the apparent diffusion coefficient (D^a) and apparent chloride content (C_0) as a function of exposure time at Leixões harbour

Time [month]	$D^a \times 10^{12}$ [$m^2 \cdot s^{-1}$]	C_0 [% weight of concrete]	$D^a \times 10^{12}$ [$m^2 \cdot s^{-1}$]	C_0 [% weight of concrete]
Concrete		Concrete + A		
6	19	0.31	6.7	0.19
12	11	0.29	2.5	0.27
18	4.0	0.51	5.8	0.22
24	6.9	0.32	1.8	0.35
Concrete + B		Concrete + C		
6	16	0.041	4.0	0.098
12	6.1	0.099	5.1	0.19
18	9.6	0.13	3.4	0.19
24	7.4	0.23	3.9	0.25
Concrete + D		Concrete + E		
6	16	0.032	-	0.014
12	-	0.020	-	0.053
18	12	0.057	11	0.059
24	15	0.067	11	0.071
Concrete + H		Concrete + I		
6	-	-	11	0.013
12	7.1	0.049	4.1	0.047
18	10	0.055	10	0.041
24	5.9	0.044	-	0.030

crete slabs over the time is also presented.

It can be observed that the presence of the coatings over the concrete surface have the following effects:

- reduction of the surface apparent chloride content (C_0);
- delay in the naturally occurring reduction [18, 22] of the concrete diffusion coefficient D^a over the time.

The overall ranking of effectiveness of the coatings in reducing chlorides rate of permeation, evaluated from the decrease in the value of C_0 , was:

$$H \approx I > D \approx E > B > C > A$$

5. CONCLUSIONS

The main conclusions that can be drawn from this study are the following:

1. Coatings applied on concrete surfaces provide different degrees of protection against chloride intake. Among the studied products, organic solvent based coatings were the more effective, as assessed either in laboratory or in field tests.

2. The ranking of the coatings effectiveness against permeation of water agrees with the laboratory chloride permeation data.

3. The maximum value for the water permeability coefficient proposed by CEN ($w < 0.1 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-0.5}$) does not seem to be enough to guarantee that the coatings will be adequate for the protection of concrete against chloride ingress. In fact, by the test field data it can be seen that coating B with w ten times lower than the min-

imum specified ($0.011 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-0.5}$) does not protect efficiently the concrete against chlorides.

4. The overall ranking of the effectiveness of the coatings against permeation of chlorides evaluated in the laboratory by using a cell permeation test reasonably agrees with test field data.

5. Analysing both field and laboratory data it can be suggested that the coating sodium chloride mass transport coefficient, evaluated by the cell permeation method, must be less than $10 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$, if the intended use is the ingress protection against chlorides.

6. As can be observed in the results presented in Table 2, the main effects of the presence of coatings on concrete are:

- Reduction of the apparent surface chloride content, C_0 , meaning that the presence of the film coating simulates the exposure of the concrete to a less aggressive environment, which can lead to a delay in the velocity of penetration of chlorides;
- Modification of the evolution of the concrete chloride diffusion coefficient, D^a . The decrease of the concrete diffusion coefficient along the exposure time is slower in the painted concrete than in the unpainted one: the more impermeable the coating is, the slower this reduction is.

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