International RILEM Workshop on Integral Service Life Modelling of Concrete Structures
5-6 November 2007, Guimarães, Portugal

EVALUATION OF POLYMERIC COATINGS AND PRIMERS AGAINST CHLORIDE INGRESS IN CONCRETE

José Aguiar [1], Luc Schueremans [2], Pedro Moreira [1], Aires Camões [1] and Dionys Van Gemert [2]

(1) Department of Civil Engineering, University of Minho, Portugal

(2) Department of Civil Engineering, KU Leuven, Belgium.

Abstract

Nowadays, it is common knowledge that the biggest degradation of concrete is caused by outside to inside actions. Penetration of moisture, active gases and aggressive ions, as well as mechanical, physical and chemical causes frequently act together. A low porosity and low permeability of concrete to penetration of moisture and gases are the first lines of defence against several deterioration mechanisms. One of the possible ways to protect the concrete is using coatings and primers that act as a barrier against the environment.

The effect of polymeric coatings and primers on the prevention of chloride ingress in concrete is studied. The chloride diffusion coefficients are determined by means of the CTH rapid method, in which chloride flow is forced with an electrical potential difference. Three polymers – silicone, acrylic and epoxy – were applied on normal and high performance concretes. The measured diffusion coefficients are compared. The importance of the measured differences is visualised by a life time prediction of the different combinations of concretes and polymers, with a concrete cover of 50 mm. Although all polymers improved the system performance against chloride ingress, the best results were found for the epoxies used.

1. INTRODUCTION

It is now accepted that the durability of 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 most of the times the only responsible for the corrosion protection of the reinforcement. Surface treatments act as a barrier between the environment and the concrete. They prevent or retard the entry of harmful substances such as water, chlorides, etc. [2]. Surface coatings with appropriate "barrier" characteristics can cut off the transportation path into concrete. The standard EN 1504-2 [3], establishes as a minimum requirement for the coated concrete ingress that the water permeability coefficient should not exceed 0.1 $kgm^{-2}h^{-0.5}$ and the CO_2 permeability should at least correspond to a s_D value of 50 m.

Concrete coatings can be applied to protect either existing or new structures. However, with a wide range of coatings available in the market, it becomes extremely difficult to choose the

right type of coating, since similar generic types are known to possess considerably different diffusion characteristics [4]. Three polymers – silicone, acrylic and epoxy – were applied on normal and high performance concretes. The measured diffusion coefficients are compared. The importance of the measured differences is visualised by a life time prediction of the different combinations of concretes and polymers, with a concrete cover of 50 mm.

2. EXPERIMENTAL PROGRAM

2.1 Materials

To evaluate the influence of cement, two types were used: a Portland cement (CEM I 42.5R) and a pozzolanic one (CEM IV/A (V) 32.5R), made with 35% of fly ash, according to EN 197-1 [5]. Table 1 presents the estimated compound composition of the cements using Bogue's expressions and Table 2 shows some physical characteristics of the selected cements. Crushed granite with a density of 2566 kg/m^3, water absorption of 2.1%, fineness modulus of 5.89 and a maximum size of 9.53 mm was used as a coarse aggregate, while crushed sand with a density of 2477 kg/m^3, water absorption of 1.36 %, fineness modulus of 3.16 and a maximum size of 4.76 mm was used as a fine aggregate in the preparation of concrete specimens. Two types of concrete were used. A normal concrete made with the two types of cement, with a water-cement ratio of 0.60 and a cement content of 320 kg/m^3. A high performance concrete made with CEM I 42.5R, water-cement ratio of 0.40 and a cement content of 500 kg/m^3.

Table 1: Estimated compound composition of the cements

Compound composition	CEM I 42.5R (%)	CEM IV/A (V) 32.5R (%)
C_3S	64.39	27.70
C_2S	5.24	16.83
C_3A	6.26	6.69
C_4AF	9.42	10.85

Table 2: Physical characteristics of the cements

Physical characteristics	CEM I 42.5R	CEM IV/A (V) 32.5R
Density (kg/m^3)	3110	2830
Blaine specific surface (m^2/kg)	3873	4292
Fineness – 45 μm (%)	3.1	2.6
Water demand (%)	28.6	31.4

Various generations of protective products have been developed to counteract the aggressive actions of the environment against concrete. After the products have been applied to the concrete surface, different systems for concrete protection can be found (Fig. 1) [6]. Concrete coatings and primers were selected to represent the following three generic types:

i. Silicone primers (S);
ii. Acrylic coatings (A);
iii. Epoxy resin coatings (E).

Each generic type was represented by two coatings from different producers. The selection is explained in [7]. Table 3 shows the properties of the selected concrete coatings and primers. All products were applied on the substrate by brush following the recommendations of the producers and after a good drying of the specimen.

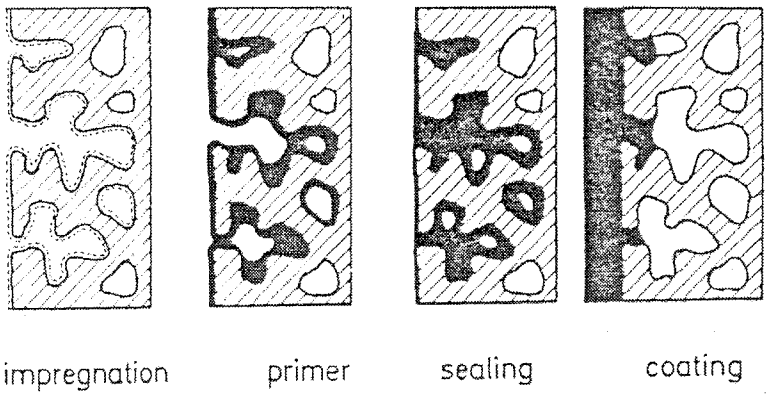


Figure 1: Definitions of systems for concrete protection [6].

Table 3: Description of the selected coatings and primers

Generic type	Silicone, SA	Silicone, SB	Acrylic, AA	Acrylic, AB	Epoxy, EA	Epoxy, EB
	siloxane resin in solvent base	siloxane resin in solvent base	acrylic resin aqueous based	acrylic resin aqueous based	two component epoxy resin	two component epoxy resin
Consistency	liquid	liquid	dense liquid	dense liquid	Dense liquid	dense liquid
Coverage rate (m^2/dm^3)	4.0	2.8	5.0	3.5	2.2	4.0
Density at 20 °C (kg/dm^3)	0.80	0.83	1.30	1.40	1.60	1.30
Brookfield viscosity at 20 °C (mPa.s)	2	11	9000	6000	1000	1500

2.2 Penetration of chlorides

The characterisation of the resistance against chlorides penetration was made with tests based on a non-steady state procedure known as CTH Rapid Method developed by Luping [8]. The depth of penetration of the chloride front is determined by a colorimetric method using silver nitrate. The diffusion coefficient is obtained using the equation given in [8].

Concrete cylinders with dimensions Ø110×230 mm were moulded. These cylinders were cut later in smaller ones with dimensions Ø110×50 mm, in order to obtain the specimens used in the tests. The paintings were applied when the concrete had 28 days. Before applying coatings and primers the concrete specimens stayed 7 days outside water, in order to guarantee that the surfaces were not in wet conditions. The paintings were only applied on one face of the cylinders. This face was the only one in contact with chlorides during the test. The instructions of the supplier of the coatings and primers were followed during all the process. The tests started 7 days after coatings and primers were applied on concrete specimens.

After the time needed for the conclusion of the test, the specimens were taken-out from the equipment and broken in two halves by tensile spitting strength test. The solution of silver nitrate was then applied on the concrete surface and the colorimetric test was made in order to measure the depth of chlorides' penetration. Five specimens of each composition were tested.

3. RESULTS AND DISCUSSION

3.1 Penetration of chlorides

The penetration of chlorides depends on the porosity of the surface. The use of coatings or primers contributes to decrease the porosity of the surface. The porosity depends on the solids volume, on the thickness and type of the product used. The CTH Rapid Method uses the current to accelerate the penetration of chlorides through the concrete surface. Higher is the porosity less will be the current that passes through the concrete surface. Epoxy resins with a reactive solvent base have good resistance to chloride penetration [9].

Table 4 and Fig. 2 present the results obtained in a non-steady state chloride penetration tests. The use of coatings and primers decreases the penetration of chlorides. In the case of the epoxy resin (ECONV and EBED) the diffusion coefficient was null.

3.2 Service life prediction

Based on the measured material properties, a service life prediction can be performed using a time dependent reliability analysis [10-11]. The reliability analysis used in this paper is applicable to concrete deterioration associated with steel corrosion initiated by the action of chloride ions. Similar analyses can be performed for other deterioration processes as long as the mathematical formulation governing the failure mechanisms is available.

It is virtually impossible to introduce a mathematical model taking into account all the variables involved in the corrosion process. To estimate the service life of a given concrete element, some assumptions need to be made. To model the chloride transport process in a porous material, it is assumed that Fick's 2nd law applies, although it is a simplified representation of reality [12-13]. Fick's second law describes the transport of chlorides in the concrete due to diffusion. In reality, the diffusion process is only valid in saturated conditions. When the pores are empty, capillary forces drag the outside solution into the concrete, bring the salts along. Other assumptions are made that are not completely valid for concrete. In the derivation of Fick's law it is assumed that the porous material is homogeneous, that the medium is non-reactive and non-adsorptive, which are not valid for concrete. Despite of the differences between the assumptions on which Fick's law is based and reality for the application intended, it is still accepted as the common model to describe chloride transport into concrete. Of course,

a similar analysis could be performed on more accurate models, as they become available. The transport model and its limitations also count for a classical deterministic analysis, and certainly is not a limitation of the probabilistic analysis.

Table 4: Chloride diffusion coefficients for different types of paintings and concretes.

References	Cement	Coating or primer	C (Kg/m^3)	w/c	D (10^{-12} m^2/s)
CONV	CEM I	-	320	0.60	14.40
IV	CEM IV	-	320	0.60	9.87
BED	CEM I	-	500	0.40	6.90
SCONV	CEM I	Silicone	320	0.60	4.68
SBED	CEM I	Silicone	500	0.40	2.04
ACONV	CEM I	Acrylic	320	0.60	6.53
ABED	CEM I	Acrylic	500	0.40	3.86
ECONV	CEM I	Epoxy	320	0.60	0.00
EBED	CEM I	Epoxy	500	0.40	0.00

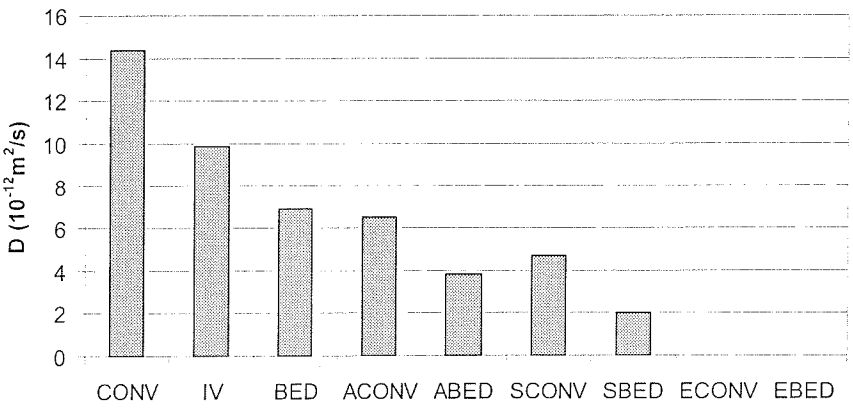


Figure 2: Diffusion coefficients in a non-steady regime for different concretes and different coatings and primers.

The Fick's 2nd diffusion law for one-dimensional chloride diffusion into concrete, takes the form:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{3}$$

in which concrete is assumed to be a homogeneous, isotropic material. When assumed that no reaction occurs between concrete and chlorides, an explicit solution of this differential equation can be obtained, using the following boundary conditions:

- $C(x,t=0) = C_0$; $0<x<\infty$ (the initial chloride concentration in the concrete mix) and
- $C(x=0,t) = C_S$; $0<t<\infty$ (the chloride concentration loading at the surface of the concrete),

$$C_i(x,t) = C_0 + (C_S - C_0)erfc\left(\frac{x}{2\sqrt{Dt}}\right) \tag{4}$$

in which $C_i(x,t)$ is the amount of chlorides at time t, at a distance x from the concrete surface and erfc() is the error function. A reliability analysis provides a means to evaluate the probability of failure of a component. The term component describes a structure or a structural element whose limit state function is defined in terms of a single function known as the limit state function. In the present problem, where only the diffusion coefficient D is considered to be a random variable, the limit state function g(D) can be written as:

$$g(D) = C_T - C(D) \tag{5}$$

where C_T is the threshold chloride concentration and C(D) is the chloride concentration at a distance x from the exposed surface at time t. With the aid of the cumulative density function (CDF), the failure probability can be written as:

$$P_f = P(C > C_T) = 1 - F_C(C_T) \tag{6}$$

in which, $F_C(C_T)$ is the cumulative density function of C. Due to the one-to-one relation in between C and D, the failure probability can be rewritten into:

$$P_f = P(C > C_T) = P(D > D_T) = 1 - F_D(D_T) \tag{7}$$

in which $F_D(D_T)$ is the cumulative density function of D and D_T is the limit value for the diffusion coefficient found by the inverse relation of Fick's 2nd law:

$$D_T = f^{-1}(C_T) \tag{8}$$

Assuming the diffusion coefficient as a lognormal distribution, the exceedence probability is consequently obtained explicitly as:

$$P_f = P(C > C_T) = 1 - \phi\left(\frac{\ln(D_T) - \lambda_D}{\xi_D}\right) \tag{9}$$

where λ_D and ξ_D are the parameters of the lognormal distribution and ø(D) is the standard normal distribution function.

The statistics of the diffusion coefficients presented in Table 4 are summarized in Table 5. In real concrete structures the standard deviation and the variation coefficient will increase. Assuming the following boundary conditions: C_0=0.1%Cl^-/cem; C_S=1.05%Cl^-/cem; and C_T=0.7%Cl^-/cem, and considering 50 mm as the depth at which the reinforcement bars are located from the surface, the resulting service life prediction values are given in Fig. 3, for a probability of failure of 0.10, corresponding with a reliability index (beta) equal to 1.28, which is close to the target value 1.5, preset in the European standard EN 1990 [14]. Since the concrete types ECONV and EBED have a diffusion coefficient equal to zero in all experiments performed, the service life prediction will result to be infinite. This of course assumes that there is no deterioration related to the epoxy coating, due to abrasion in real and eventual harsh environments. Additional decrease of the service life related to deterioration of the coatings or primers is not accounted in none of the protected concretes covered in this analysis.

The second product with best service life predictions was the silicon primer (SCONV and SBED). This primer in combination with a high performance concrete (SBED) showed an expected service life of about 73 years. With a conventional concrete (SCONV), the expected service life decreases to about 36 years. The high performance concrete showed an expected service life of about 20 years. This shows that a good concrete could be a good solution to increase significantly the service life. The acrylic coatings (ACONV and SCONV) had the

worst performance of the protected concretes. However, the expected service life for a high performance concrete with an acrylic coating is about 35 years. The use of a conventional concrete with an acrylic coating has a predicted service life of about 25 years.

Table 5: Summary statistics of diffusion coefficients.

Reference	Average (10^{-12} m²/s)	Standard deviation (10^{-12} m²/s)	Variation coefficient (%)
CONV	14.4	5.23	36.32
IV	9.87	1.58	15.97
BED	6.9	1.17	16.98
SCONV	4.68	0.16	3.36
SBED	2.04	0.19	9.54
ACONV	6.53	0.48	7.33
ABED	3.86	0.89	23.13
ECONV	0	0	-
EBED	0	0	-

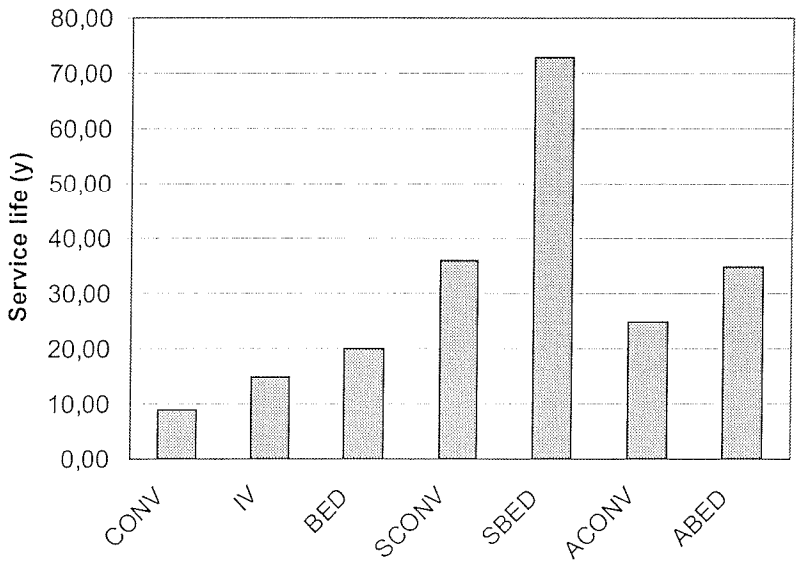


Figure 3: Variation of predicted service life with the different types of concrete and different types of coatings and primers.

4. CONCLUSIONS

The selected coatings and primers proved to be effective against chloride ingress in concrete. The diffusion coefficients of the chlorides decreased and the service life prediction values increased significantly for the protected concretes. The best used product was the epoxy coating. The results and theoretical service life predictions show that conventional concrete is not appropriate for use if chloride induced corrosion is to be expected. A protective treatment will be needed in most cases.

REFERENCES

[1] Kreijger, P. C., 'The skin of concrete. Composition and properties', *Materials and Structures*, 17 (1984) 275-283.
[2] Pfeifer, D.W. and Scali, M.J., 'Concrete Sealers for Protection of Bridge Structures', (Department of Transportation, NCHRP 244, Washington D.C., 1981) 138 p.
[3] European Committee for Standardisation, 'EN 1504-2, Products and systems for the protection and repair of concrete structures. Definitions, requirements, quality control and evaluation of conformity. Part 2: Surface protection systems for concrete', (CEN, Brussels, Belgium, 2004).
[4] Hawkins, P. J., 'The use of surface coatings to minimize carbonation in the Middle East', in Proceedings of 1st International Conference on Deterioration and Repair of Reinforced Concrete in the Arabian Gulf, (Bahrain, 1985) 273-285.
[5] European Committee for Standardisation, CEN, 'EN 197-1, Cement - Composition, Specifications and Conformity Criteria for Common Cements', (Brussels, Belgium, 2000).
[6] Sasse, H. R. and Fiebrich, M., 'Bonding of polymer materials to concrete', *Materials and Structures* 16 (1983) 293-301.
[7] Moreira, P. M., Aguiar, J. B., and Camões, A., 'Systems for superficial protection of concretes', in Proceedings of the International Symposium Polymers in Concrete, (University of Minho, Guimarães, Portugal, 2006) 225-236.
[8] Luping, T., 'Chloride transport in concrete, measurement and prediction', Doctoral Thesis, (Chalmers University of Technology, Gotemborg, Sweden, 1996).
[9] Almusallam, A., Khan, F. M. and Maslehuddin, M., 'Performance of concrete coatings under varying exposure conditions', *Materials and Structures* 35 (2002) 487-494.
[10] Schueremans, L., Van Gemert, D. and Giessler, S., 'Chloride penetration in RC/structures in marine environment – long term assessment of a preventive hydrophobic treatment', *Construction and Building Materials* 21 (2007) 1238-1249.
[11] Clifton, J. R., 'Predicting the service life of concrete', *ACI Materials Journal* 90(9) (1993) 661-671.
[12] McPolin, D., Basheer, P. A. M., Long, A. E., Grattan, K. T. V. and Sun, T., 'Obtaining progressive chloride profiles in cementitious materials', *Construction and Building Materials* 19 (2005) 666-673.
[13] Costa A. and Appleton J., 'Chloride penetration into concrete in marine environment – Part II: Prediction of long term chloride penetration', *Materials and Structures* 32 (1999) 354-359.
[14] European Committee for Standardisation, CEN, 'EN 1990, Eurocode. Basis of structural design', (Brussels, Belgium, 2002).