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Evaluation of the Water Repellent Treatment, Applied as Chloride Barrier on a Quay-Wall at Zeebrugge Harbor

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Abstract

Chloride ingress is one of the most important causes of corrosion of the reinforcement in concrete structures such as on-shore constructions in marine environment. Those structures can be protected by means of a protective coating or by a water repellent agent. The effectiveness of water repellent agents is being studied in the Reyntjens Laboratory. Based on experimental results, it was decided in 1993 to apply IBTEO (iso-butyl-tri-ethoxy-silane) on the quay-wall of the new container terminal at Zeebrugge Harbor, Belgium. In 1996, a research program was executed to evaluate the effectiveness of the treatment after 3 years of exposure in the real marine environment of the North Sea Coast.

The results of this research program are presented, as they provide a middle-long term record to evaluate the effectiveness of the water repellent agent. A probability method for interpretation of the test results and prediction of the service life of the quay-wall is proposed and updated. The method is extended in order to serve as a tool for periodical evaluation. The effectiveness of the protective system, the durability of the concrete structure and the executed quality control will be discussed by means of this case study.

Keywords: chlorides, iso-butyl-tri-ethoxy-silane, probability method, durability

1 Introduction

Chloride ingress is one of the most important actors in the corrosion process of concrete reinforcement rods. Especially for off-shore and marine constructions the exposition to chlorides from sea water and marine air play an important role. The ingress of chloride ions into the pores of the concrete is caused by diffusion through the pores if they are filled with water or capillary suction if the pores are empty. When the chloride ions reach the reinforcement bars, the passivating oxide layer may be depassivated, which initiates the local corrosion of the rods.

The chlorides in the concrete either come from the components of the fresh mix or from external contamination. The chlorides that stand for the corrosion risk of the reinforced concrete structure are the free chlorides in the pore water and the water soluble salts (Salt of Friedel) that act as a stock of free chlorides [1,2].

To evaluate the risk caused by chloride ingress, service life predictions are very important, both for existing and planned structures [3]. The time dependent reliability method, as proposed and updated in this paper, uses the chloride profiles of the free chlorides as measured at different locations on the container quay-wall and at different depths from the concrete surface. Therefore cores were taken as well on locations treated with a water repellent agent as on non-treated locations. For each point of the concrete cores where the chloride concentration is measured, a value of the diffusion coefficient D_i can be back-calculated using the inverse relationship of Fick's 2^{nd} law. These values are used to estimate the probability density function of the diffusion coefficient D at the different locations. Once the probability density function D is estimated, a reliability analysis is performed to calculate the service life prediction. This enables to evaluate the effect of a preventive hydrophobic treatment. To validate the model, its sensitivity towards the major variables is calculated and discussed. Based on the set of material properties gained from the in-site test program, a range of major variables is set to obtain a tool for evaluation of the service life of the concrete structure as to chloride ingress. Finally, a model to account for the possible degradation of the effectiveness of the hydrophobic treatment is proposed and illustrated.

2 Quay-wall of the container terminal at Zeebrugge

In order to increase the durability of the concrete, it was decided to apply an hydrophobic treatment on the quay-wall of the container terminal at Zeebrugge. The construction of the container terminal at Zeebrugge was ordered by the Ministry of the Flemish community, Sea-Harbor Division and finished in 1993. Figure 1 gives a general view of the quay-wall, constructed on top of cylindrical sunk down reinforced cells (caissons). For practical reasons of ease of application it was decided to apply an hydrophobic treatment with highly concentrated solvent-free compounds based on iso-butyl-tri-ethoxy-silan, in order to prevent it for damage caused by chloride penetration, pitting corrosion and alkali-aggregate-reaction.

By means of a preliminary research program [4,5], the effectiveness of the hydrophobic agent was evaluated. The production, application and working mechanism of silanes are outlined elsewhere [2].

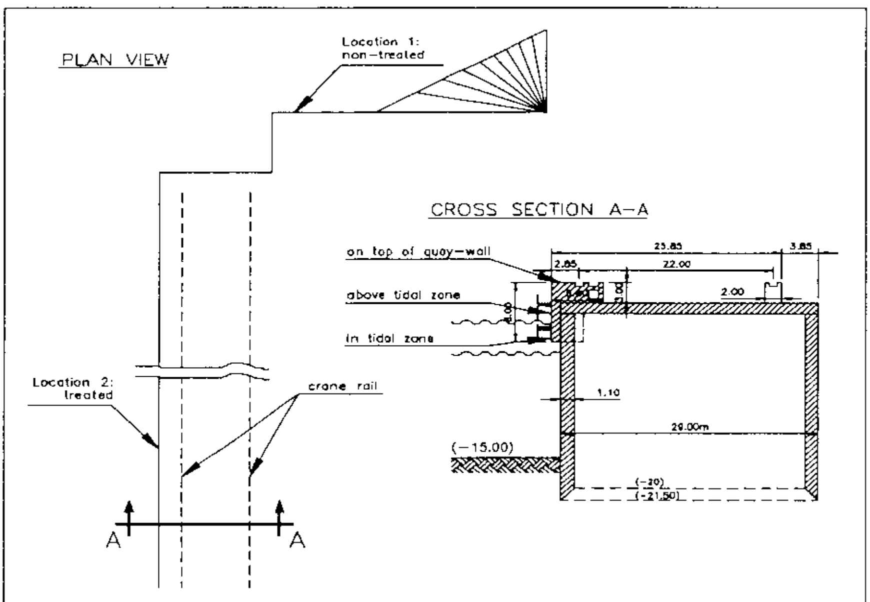

Figure 1: Plan view and cross section of the quay-wall and locations of the cores

3 Testing program

In 1996, the in-service performance of the IBTEO water repellent was evaluated [6], [7] on cylindrical cores taken at different locations in the quay-wall (see fig. 1): treated (location 2) and non-treated (location 1) locations, in the tidal zone, above water level and on top of the quay-wall.

To get a global view of the effectiveness of the hydrophobic agent, following characteristics were measured: penetration depth, porosity, pH at following depth: 0-9 mm, 11-20 mm, 40-60 mm, carbonation depth, compressive strength, cement content and chloride content. The characteristics relevant for this paper are summarized in table 1. A full report can be found in earlier [5], [8].

The chloride content was measured at the following depth: 0-9 mm, 11-20 mm, 40-60 mm. The content profiles of water soluble chlorides are shown in figure 2. The chloride contents were determined by means of wet chemical analysis, according to the Belgian Standard NBN B15-257. The chloride content, obtained by wet chemcal analysis, equals the amount of

Table 1: Material properties and water-soluble chloride content

	Core no	**n [v%]**	**Dry density [kg/m^3]**	**amount of cement [kg/m^3]**	**%Cl$^-$/ cem at x=4.5 mm**	**%Cl$^-$/ cem at x=15.5 mm**	**%Cl$^-$/ cem at x=50 mm**
Non treated location 1 figure 1	A1	17.48	2157	284	2.77	3.44	2.18
	A2				2.07	3.22	1.84
	A3	14.57	2232		1.91	2.28	1.44
	A4	14.76	2224		3.35	2.36	1.51
treated location 2 figure 1	B5	15.66	2234	260	2.24	1.23	0.38
	B6				1.31	1.66	0.29
	B7	17.38	2193		1.75	0.94	0.32
	B8	16.70	2197		1.64	1.07	0.36
Treated on top of quay-wall	C9	14.86	2236		0.71	0.53	0.45
	C10				0.64	0.64	0.44
mean value		16	2200	272			

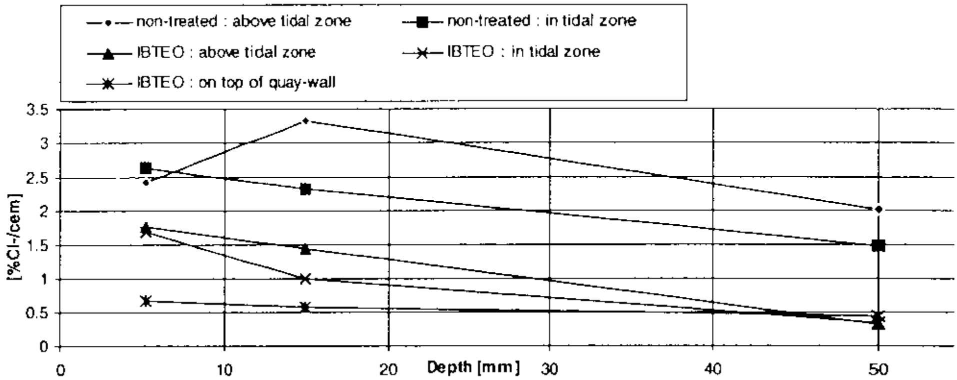

Figure 2: Water-soluble chloride content by weight of cement at different depths in the cores

free chlorides and a great deal of the chlorides, bound under the form of the Salt of Friedel which dissolves in the water during extraction [9]. In fact, these water soluble chlorides mean the real danger for corrosion of the reinforcement [6].

The relation water soluble to acid soluble chlorides amounts 94% in the executed tests [5]. Thus, the amount of insoluble chlorides is very restricted as the greater part of chloride loading is caused by the external contamination, i.e. the marine environment. It can be observed that the chloride content in the non-treated zones is significantly higher than in the treated zones. The absence of an effective barrier, combined with the relatively high porosity, allowed the chlorides to penetrate very deep in the concrete in a relatively short time period. On the contrary, the chloride content in the treated zones are still at acceptable level, and combined with the low carbonation depth, they present no danger for reinforcement corrosion.

4 Service Life Prediction, a time dependent reliability analysis

Based on the measured material properties and chloride profiles, a service life prediction can be performed using time dependent reliability analysis [10]. It is becoming increasingly important to be able to predict the service life of concrete for new constructions and/or concrete structures in-service

[3] (development of life-cycle cost models, demand of increased service life, increased use of concrete in harsh environments, cost of rebuilding and maintenance, ...).

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 are available.

With the present state of knowledge, 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, many 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. Fick's second law describes the transport of chlorides in the concrete due to diffusion. As seen before, the diffusion process is only valid in saturated conditions. When the pores are empty, capillary forces drag the outside solution into the concrete, bringing the salts along. Other assumptions are made that are not 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 [11].

Despite of the differences between the assumptions on which Fick's law is based and reality for the application intended, it provides the only way available to model chloride diffusion into concrete. A similar analysis could be performed on more accurate models, as they become available.

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

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

in which concrete is assumed to be a homogeneous, isotropic material. When assumed that no reaction occurs between the 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 due to the marine environment),

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

in which $C_i(x,t)$ is the amount of chlorides on the time t at a distance x from the concrete surface.

A reliability analysis provides a means to evaluate the probability of failure of a component. The term component describes a structure or structural element whose limit state function is defined in terms of a single, continuous function known as the limit state function [10]. In the present problem, where only the diffusion coefficient D is considered to be random, the limit state function g(D) can be written as:

$$g(D) = C_T - C(D) \qquad (3)$$

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.

The function g(D) - the limit state function - is positive only if the concrete element is in a 'safe' state, i.e. the chloride concentration at the reinforcement (at a distance x from the concrete surface) is less than the threshold concentration. Having the probability density function of the diffusion coefficient D, the probability that the chloride concentration C_T is exceeded can be expressed as:

$$P_f = P(C > C_T) = 1 - F_C(C_T) = P(D > D_T) = 1 - F_D(D_T) \qquad (4)$$

where $F_C(C_T)$ is the cumulative distribution function of C, and $F_D(D_T)$ is the cumulative distribution function of D, which are related to each other by the one-by-one relationship between C en D. The threshold diffusion coefficient D_T can be obtained by the inverse relation of Fick's second law: $D_T = F^{-1}(C_T)$.

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

$$P_f = P(C > C_T) = 1 - \Phi\left(\frac{\ln(D_T) - \lambda_D}{\xi_D}\right) \qquad (5)$$

where λ_D and ξ_D are the parameters of the lognormal distribution and $\Phi(D)$ is the standard normal cumulative distribution function.

5 Realization of the diffusion coefficient D

With the chloride profiles of the concrete samples exposed during a given period, the diffusion coefficient can be back-calculated using an inversion of Fick's 2^{nd} law (eq.2). In the inversion of Fick's second law, following boundary conditions were used: $C_0 = 0.03$ % Cl^- and C_S 7% Cl^-/H_2O [2].

Table 2 gives the mean value $\mu(D)$ and the standard deviation $\sigma(D)$ as well as the coefficient of variation $cov(D) = \sigma(D)/\mu(D)$ for the groups of cores, taken at different locations. Remarkable is the diffusion coefficient of the non-treated zone to be nearly an order of magnitude bigger than in the treated locations.

6 Service life prediction for the container terminal

With the computed parameters of the lognormal probability distribution for the diffusion coefficient D, the service life can be predicted using the reliability analysis as outlined before. A corrosion initiation mode can be characterized in a simplified way by specifying a threshold chloride concentration beyond or above which corrosion would start. The reliability analysis is performed for the threshold chloride concentrations that equals 0.4 percent per weight of cement and 0.7 percent per weight of cement. As the free chlorides mean the real danger for corrosion, only the water soluble chlorides (table 1) were taken into account.

For a conventionally taken probability of failure of 50 percent ($P_f = 0.5$) [2,11], table 2 shows the time it will take in years for the threshold chloride

Table 2: Diffusion coefficients and service life prediction (SLP)-values for Pf = 0.5 at the different locations

SLP-values for $P_f = 0.5$ at x = 120 mm	$\mu(D)$ [$cm^2/s \times 10^{-8}$]	$\sigma(D)$ [$cm^2/s \times 10^{-8}$]/ (cov(D)[%])	SLP [years] C_T=0.4%Cl^-/ cem	SLP [years] C_T=0.4%Cl^-/ cem
A (non-treated)	9.64	7.0 / (72.5)	7.6	12.6
B (treated with IBTEO)	1.18	1.0 / (88.1)	61	105.1
B /treated with IBTEO) on top of quay-wall	1.32	1.7 / (128)	70	123.3

concentration to reach the reinforcement. The values listed in table 2 reflect the assumption that the reinforcement is located at 120 mm from the exposed surface as could be measured from the taken cores. The service life prediction (SLP) values in years are given in the assumption that no erosion of the concrete surface takes place, which would remove the water repellent and thus its beneficial effects on chloride penetration.

7 Most influencing parameters

7.1 Influence of x an C_T on SLP-values

Figure 3 shows the influence of the concrete cover thickness with regard to the obtained service life. The calculations are outlined for the above mentioned cases: non-treated (A), treated with IBTEO in the tidal zone (B), treated with IBTEO on top of the quay-wall (C). The dashed lines represent the results obtained with a threshold chloride concentration of 0.7 % Cl^-/ cem. The threshold value has a great influence on the calculated service life. It nearly doubles the SLP-values. On the other hand, the influence of the application is becoming bigger with higher concrete coverage values. This relation is well approximated with a quadratic curve.

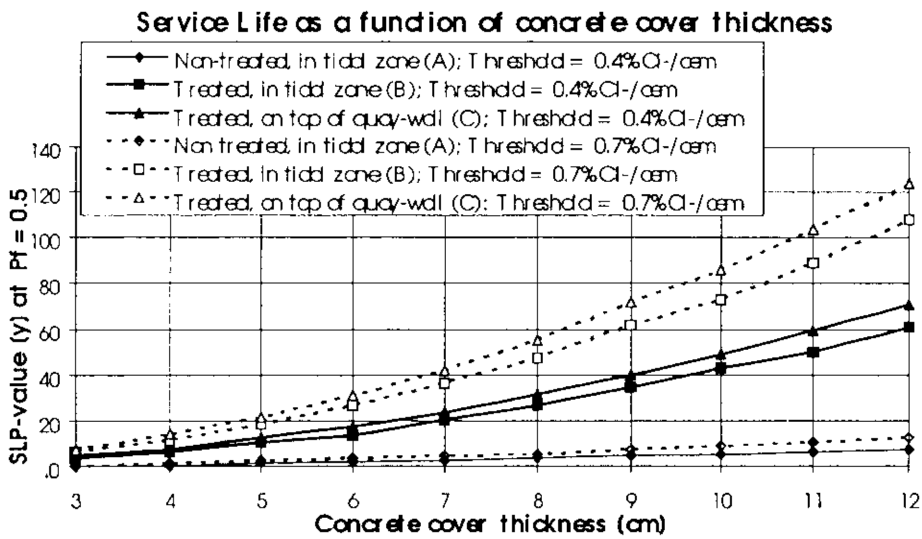

Figure 3: Influence of the concrete cover thickness on the SLP-values

The big differences in obtained SLP-values are due to the order of magnitude difference in D values between treated and non-treated, and due to the wide scatter in the obtained D values (cov varies from 72.5 % up to 128 %).

7.2 Influence of D (mean, cov), C_0, C_S and C_T

Figure 4 lists the influence of the main parameters involving the calculated SLP-values, using Fick's second law (eq. 2): D (μ,σ), C_0 en C_S and C_T. For the calculation of the influence of these parameters, the figure starts from the following set of material properties, see table 3, which is handled as the basic set in the next paragraphs. These values are mean values as obtained from the experimental research (table 1 : mean value of dry density [kg/m^3] and of porosityn [v%]).

It is clear from all 4 figures that a higher threshold value C_T will lead to elongated SLP-values.

The influence of the mean value of the diffusion coefficient flattens out for bigger values. On the contrary, the influence on the calculated SLP-values for low mean values is important. It behaves asymptotically as the mean value approaches zero. This is clear, because, as a result, no diffusion will take place, what leads to an infinite service life.

The influence of the coefficient of variation of the diffusion coefficient is comparable. Remember equation 5 (eq. 5) that is used to calculate the probability of failure. As the cov will tend to zero the standard deviation will also tend to zero, which will lead to a probability of failure equal to zero, thus an infinite service life prediction value would be obtain,ed.

The influence of the initial Chloride concentration C_0 is least important of the mentioned variables. Maximum difference in predicted service life is about 7 years, a period that can easily be won by taking care the initial concrete mix contains least possible free chlorides.

Table 3: Basic set of main variables

Dry density [kg/m^3] n [v%]	**2200** **16**	**Distance of reinforcement to surface : x [cm]**	**5**
C_0 [% Cl^-/cem]		Diffusion coefficient : μ(D) [$cm^2/s \times 10^{-8}$]	1
C_S [% Cl^-/H_2O]		cov (%)	100

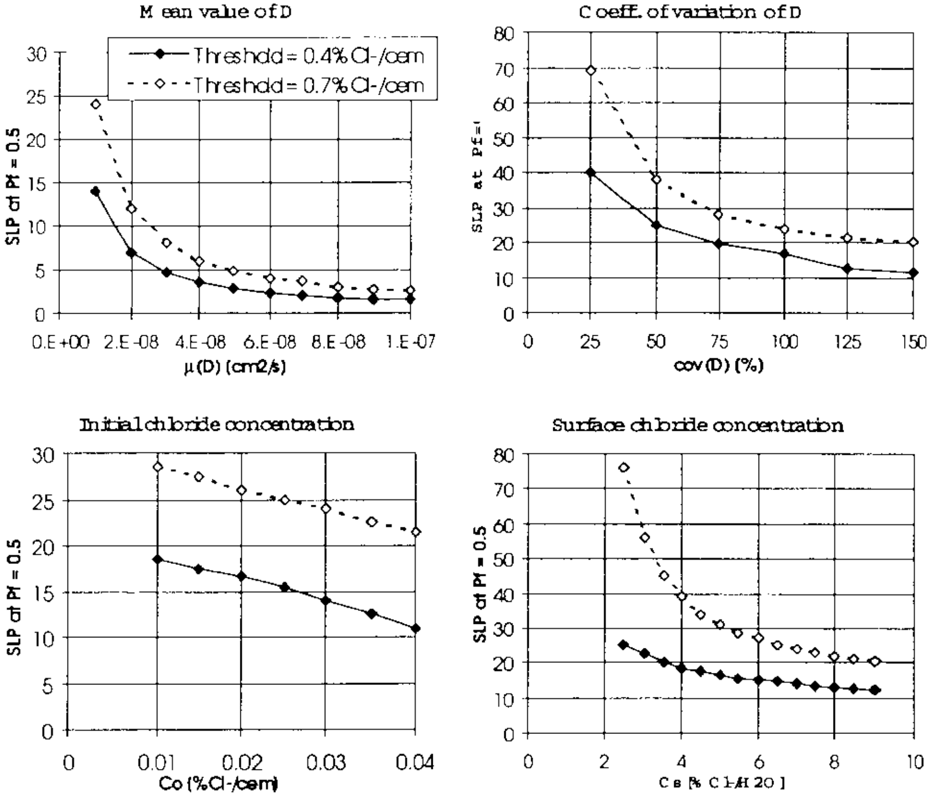

Figure 4: Influence of D (mean, cov), C0, CS and CT on the SLP-values

The surface chloride concentration is of major importance. It is the engine after the diffusion process. Indeed, the bigger the difference in concentration, the faster the diffusion process will run, the smaller the service lives obtained. As the surface concentration approaches values that are similar to the initial values, the diffusion process will stop. In the limit, when it equals the amount of initially present chlorides in the concrete mix, service life would be infinity. This is shown by the asymptotic behavior near the y-axis.

8 Evaluation graphs for practice

Based on the assumptions made before and taken into account the different sensitivities of the major variables, a graph is set up to evaluate the service life of the concrete structure, my means of the obtained diffusion coefficient's D. These are calculated on the basis of the chloride profiles, as outlined in paragraph 6. By means of this graph one is able to predict the service life of the concrete structure due to chloride ingress, based on the measurement of the chloride profiles and the depth of the reinforcement bars from the surface. The service life is calculated for a probability of failure that equals 0.5, as mentioned before. The SLP-values are outlined as a function of the concrete cover thickness.

Without loss of generality, the graphs will be configured for the basic set of material properties and boundary conditions as outlined in table 3. These are mean values, valid for this specific concrete structure. A completely analogue set of graphs could be configured for another set of variables. The graphs show the SLP-values as a function of the thickness of the concrete cover. Parameter in here is the diffusion coefficient (D) and the threshold chloride concentration (C_T). The mean value - $\mu(D)$ - as well as the coefficient of variation - cov(D) - were varied along a range covering the experimental results, see table 2.

Following values are implemented :

- for the mean value following $\mu(D)$: $1.0\ 10^{-8}\ cm^2/s$, $5.0\ 10^{-8}\ cm^2/s$, $10.0\ 10^{-8}\ cm^2/s$,
- for the coefficient of variation cov(D): 75%, 100%, 125 %,
- for the chloride threshold value C_T: 0.4 %Cl^-/cem, 0.7 %Cl^-/cem.

The result is outlined in figure 5. Left part of the figure shows the results for $\mu(D) = 1.0\ 10^{-8}\ cm^2/s$, the right part for the other two values. The full lines are used to indicate $C_T = 0.4$ % Cl^-/cem, the dashed lines to indicate $C_T = 0.7$ % Cl^-/cem.

The above mentioned results are only valid for the outlined failure mode: chloride penetration based on a diffusion process, discribed by Fick's 2nd law. Note that the results in this figure only appoint the time at which the chloride concentration reaches the reinforcement bars. This period states the initiation period at which the reinforcement starts to corrode. The model does not include the propagation period.

Therefore, the chloride penetration failure mode might not be crucial anymore for high predicted values (100 years and more). Other failure modes might become more crucial over that period (erosion, earthquakes,..). Also, possible degradation of the water repellent agent has not been taken into account.

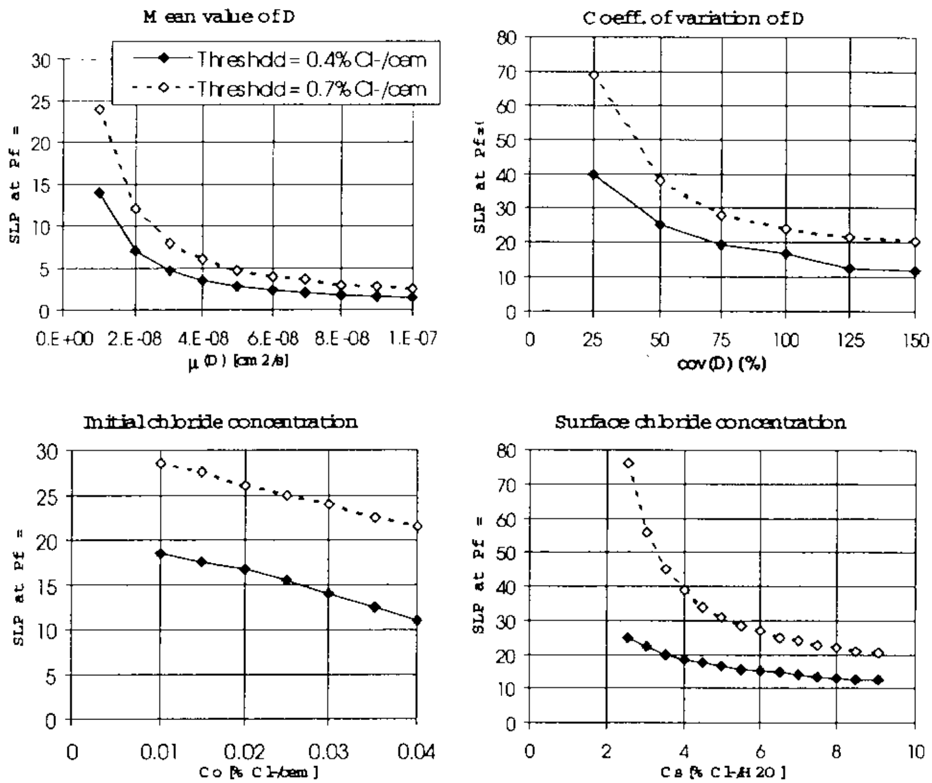

Figure 5: Evaluation graph for inspection based on measured chloride profiles (Concrete cover 120 mm)

9 Modeling degradation of the effectiveness of the water repellent agent

Degradation of the water repellent agent could be modeled by making the obtained diffusion coefficient time dependent. As no experimental values are available for the moment to calibrate the model this paragraph is only meant for the sake of completeness and illustration. The extra research program after 5 years of in service exposure will provide further data that can also be used for a first estimate of possible

Assume that the effectiveness of the water repellent agent deteriorates with time due to environmental influences. This will influence the obtained diffusion coefficient D according to [12]:

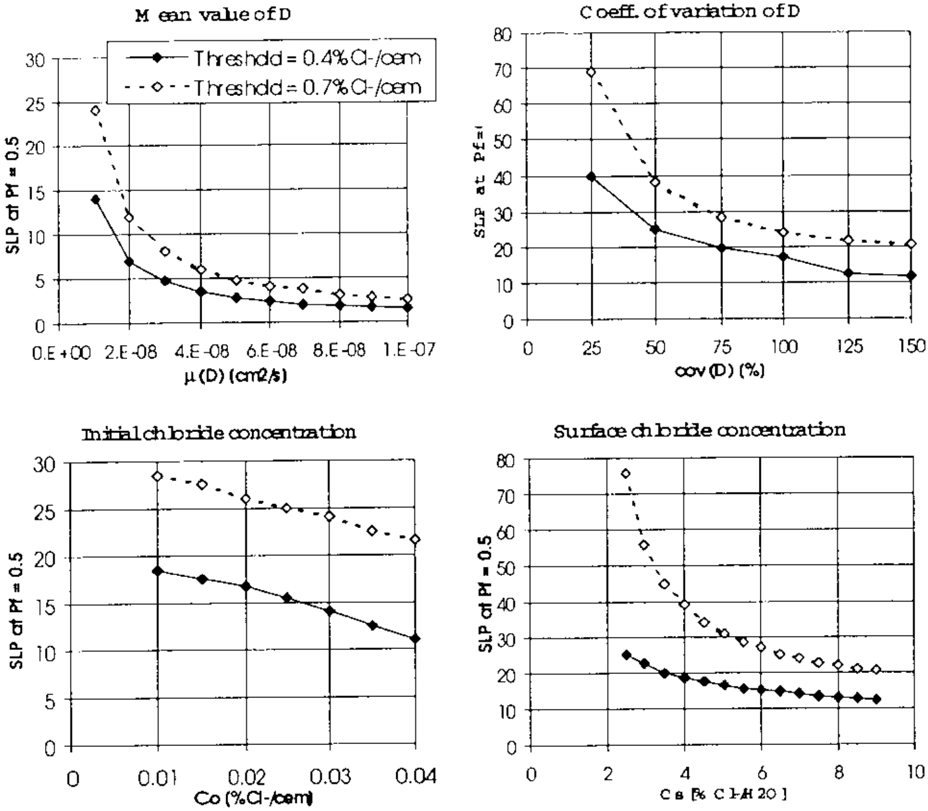

Figure 6: Modeling degradation, influence of the shape of the degradation function and of the rate of degradation

$$D(t) = D_0 \cdot g(t) \tag{6}$$

in which D(t) = the diffusion coefficient at time t; D_0 the original value of the diffusion coefficient in the undegraded (original) state, and g(t) de degradation function. Many shapes of the degradation function have been proposed [12] - see figure 6 -, that could also model the degradation of the effectiveness of the water repellent agent. Figure 6 - left - shows the effect of the shape of the degradation function. The calculations where performed for the above mentioned basic set of variables, table 3. Without loss of generality, g (20) is set equal to 1.25, meaning 25% degradation after 20 years of service, to obtain a value for the parameter a. Figure 6 - right - shows the influence of the degradation rate on the SLP-values. In that, the linear degradation function was used. As a reference, the non-degraded function is also shown in both figures.

10 Conclusions and further research needs

An in-service test program and a service life prediction method, based on a time-dependent reliability method, were presented. The in-service test program - executed after 3 years of in-service exposure - showed the effectiveness of the highly concentrated, solvent-free compound based on isobutyl-tri-ethoxy-silane as a water-repellent agent. Although the used time dependent reliability analysis only takes into account the diffusion process in the concrete, mathematically translated by Fick's second law, it proves the impact of this preventive protection method.

The time dependent reliability method gives graphs of service life prediction (SLP)-values, that can be used to verify the estimated service life. The sensitivity of the reliability analysis towards its major variables was outlined and discussed. Also, a model for treating the possible degradation of the effectiveness of the water repellent agent was proposed and illustrated, although it could not be calibrated yet, by lack of long-term data. Extra cores have already been taken and will be used to update and control the model, as well as to provide first estimates to account for possible degradation in the time-dependent method.

This positive result should encourage engineers to consider a hydrophobic treatment as a full phase in the construction process. On the other hand it should stimulate them to prescribe inspection on a regular time basis in a global maintenance plan, as periodic inspection enables to verify whether the required level of safety is still met, and the durability of the concrete is guaranteed during the preset service life.

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