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Durability of Water Repellents in a Marine Environment

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Abstract

The paper deals with the quay-wall of the new container terminal at Zeebrugge Harbor, Belgium, that has been protected against chloride ingress. For this purpose a water repellent agent based on isobutyltriethoxysilane was applied immediately after construction in 1993 and evaluated in a preliminary research program. To assess the effectiveness of the water repellent treatment in service, three subsequent on-site surveys were conducted in 1996, 1998, and 2005. The obtained data are used to feed the deterioration models related to chloride ingress into the structure and increased carbonation depth. As a result, the failure probability for the durability limit state function related to the preset service life is estimated. The latter is compared with general accepted target failure probabilities. Because of the relative extensive data sequence, the long-term effectiveness and thus durability of the treatment can be assessed in an objective way.

Keywords: chloride ingress, preventive treatment, service life, hydrophobisation, water repellent, durability, corrosion, silane

1 Quay-wall at Zeebrugge Harbor – on-site survey

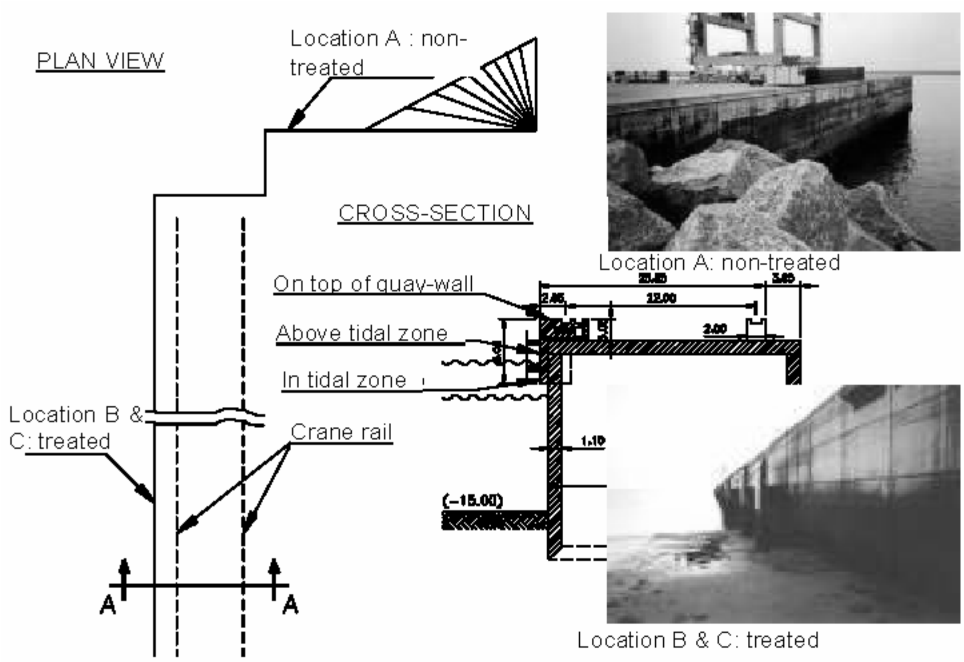

Figure 1: Plan view and cross section of the quay-wall at Zeebrugge Harbor

In order to improve the durability of the concrete it was decided to apply a hydrophobic product on the new quay-wall of the container terminal at Zeebrugge [1,2]. 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 reinforced cells (caissons). For practical reasons and ease of application it was decided to apply a solvent-free hydrophobising agent based on isobutyltriethoxysilane (Protectosil® BHN) in order to prevent the wall from damages caused by chloride penetration, pitting corrosion and alkali-aggregate-reaction.

At the construction site, the following application scheme was adopted:

- A first application of the water repellent was done immediately after remoulding, before the drying of the concrete surface and the eventual initial penetration of salt water;
- A second application was carried out 7 days after remoulding in order to obtain a deep penetration into the concrete.

The water repellent was applied by airless spraying at low pressures, using a plunger pump. The consumption was determined to be 0.35 litres per m^2 (300 g/m^2) which coincided very well with the preliminary laboratory tests on concrete cubes prepared on the construction-site.

The mid-long term effectiveness of the hydrophobic treatment has been evaluated in two subsequent on-site surveys: 1996 and 1998, after 3 and 5 years of exposure, respectively [3]. Based on these surveys, the mid-long term effectiveness could be established [4-5]. Also, the in-depth penetration was determined from the on-site samples [6].

On January 18, 2005, a third on-site survey on the quay-wall of Zeebrugge Harbor was performed after almost 12 years of exposure [7]. The goal of this survey was to update the progress of chloride penetration into the concrete caused by the seawater and to compare the results obtained at different locations built in the same period but characterised by different parameters:

- A location not treated with a hydrophobic agent in the tidal zone (location A);
- A location not treated with a hydrophobic agent above the tidal zone (location A);
- A location treated with alkyltriethoxysilane in the tidal zone (location B);
- A location treated with alkyltriethoxysilane above the tidal zone (location B); and,
- A location treated with alkyltriethoxysilane on top of the quay-wall (location C)

These results allow assessing the effectiveness of this type of preventive treatment in the long term. The values obtained after 12 years of exposure are compared with the data from former on-site surveys.

2 Testing campaign

During the on-site campaigns concrete cores (diameter = 50mm) were drilled at neighbouring positions. In general, 3 types of tests were performed on the drill cores:

- The penetration depth of the hydrophobic agent was determined based on a visual observation by wetting a fresh cracked surface;
- The carbonation depth was measured on-site before the cores were sawn into slices directly after drilling as well as in the laboratory the following day for comparison.

- Cut slices were used to determine the water soluble and acid soluble chloride contents (Figure 2) for the evaluation of the chloride penetration profile at different locations

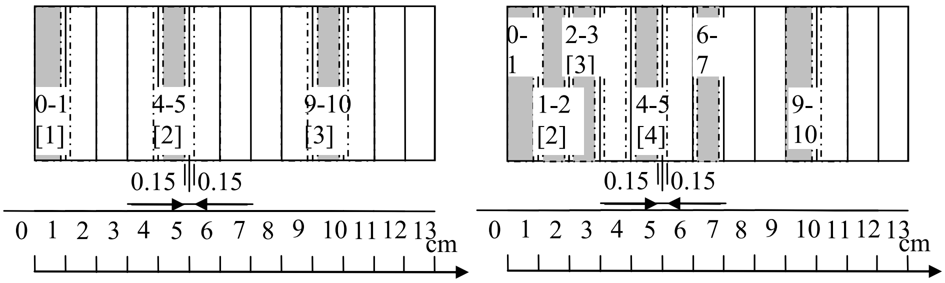

Figure 2: Schematic representation of drill cores slices for the determination of the chloride content at 3 different depths (left) or at 6 different depths (right) (zero corresponds to the outer surface)

2.1 Impregnation depth determination

At the Reyntjens Laboratory the impregnation depth for the treated concrete cores was determined visually by wetting a freshly cracked surface. The surface was obtained by cracking the concrete slices of the concrete cores. The slices had an overall thickness between 7 to 9 mm, sufficient to determine the penetration depth by visual inspection in all cases. In general, the interface between the non-hydrophobic and hydrophobic zone was clearly visible, as illustrated in Figure 3. Absorption of water in the non-hydrophobic part gave a darkening of the surface. The values for the impregnation depth varied between 1 and 6 mm, with a mean value of 3.5 mm. The individual values are summarized in Table 1, columns 2 and 3. The results of the more accurate pyrolysis-GC detection, described in patent EP 0 741 293, are summarized in the last column of Table 1 [6]. All samples showed significant concentrations of alkyltriethoxysilane even at 8 mm depth. Thus, based on this visual inspection, the hydrophobic action is still present after 12 years of on-site service.

Table 1: Penetration depth of the hydrophobising silane system

Location	Visually determined penetration depth [mm]		Concentration alkyltrialkoxysilane [%w/cem] in dependence on penetration depth 0mm 2mm 4mm 6mm 8mm [6]
	2005	1998	1998 [6]
B : above tidal zone	4-6 mm	2-6	0,14 / 0,20 / 0,08 / 0,02 / 0,00 0,13 / 0,14 / 0,16 / 0,17 / 0,06 0,07 0,18 0,19
B : in tidal zone	5-6 mm	3-5	0,12 0,04
C : on top of quay-wall	1-2 mm	1-3	0,15 0,29

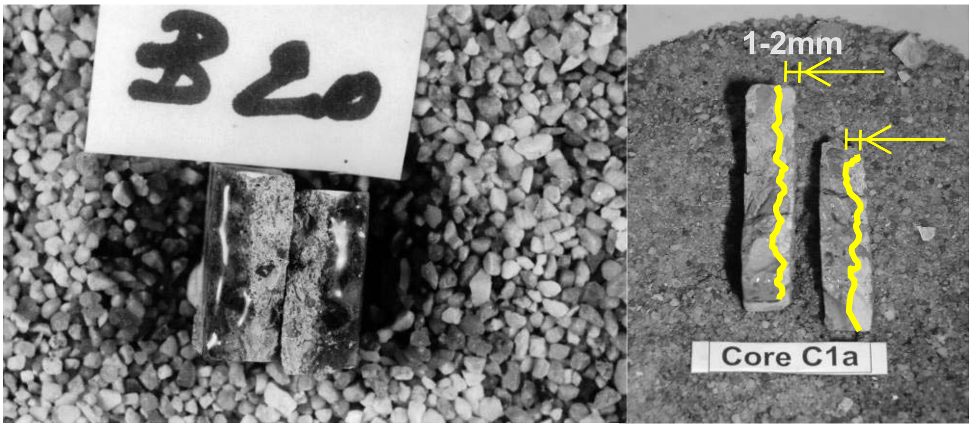

Figure 3: Example of hydrophobic action. Visual inspection by wetting a fresh cracked surface (slice thickness equals 7 mm) – core B2 (left: 1998) and core C1 (right: 2005)

2.2 Carbonation depth

The carbonation depths were determined by treating the freshly sawn surfaces with a phenolphtaleine solution (dissolved in 1% ethanol). The values obtained are listed in Table 2. The carbonation depth remained approximately zero in the non-treated location. In the treated location the carbonation depth varied from 4-6 mm in tidal zone, towards 8-12 mm above tidal zone and up to 12-16 mm on top of the quay-wall. Only the values on top of the quay-wall seem to have increased in comparison to the values of the previous campaign in April 1998 [7]. Comparing the different locations, it appears evident that the diffusion of CO_2 into the concrete is enhanced by the hydrophobic agent that prevents water to enter the concrete. The carbonation rate is strongly dependent on the amount of water present in the concrete.

Table 2: Carbonation depth in non-treated and treated locations

Location	Carbonation Depth [mm]		
	2005	1998	1996
A: non-treated			
above tidal zone	0	0-0.5	0
in tidal zone	0	0	1
B and C: treated with Protectosil® BH N			
above tidal zone	8-12	6-12	4
in tidal zone	4-6	5-10	5
On top of quay-wall	12-16	5-10	5

2.3 Chloride profiles

Two different values of chloride concentration were determined: the water soluble chloride content and the acid soluble chloride content. To determine the chloride penetration profiles the cores were sawn into slices with average thickness of 7 mm (see Fig. 3). Both types of chloride content were determined on these slices corresponding to different depths. The chloride contents were determined by means of wet chemical analysis, according to the Belgian Standard NBN B15-250 (1990) [8]. The chloride content equals the sum of the amount of free chlorides and that bound under the form of a Friedel salt ($C_3A.CaCl.10H_2O$) that is dissolved in the water during extraction. Since water soluble chlorides represent the chloride ions promoting steel corrosion, only, these are reported here. The experimental results (%Cl^-/cem) are presented in Figures 4 to 8 representing the chloride concentration at the above mentioned 5 locations as a function of time and depth. Each of the values plotted in the figures is the average of chemical analyses carried out in triplicate.

With respect to the presented chloride penetration profiles, some remarks regarding the accuracy of the experimental results are in order. The data are subject to scatter due to the heterogeneous composition of concrete, i.e., aggregates and cement paste; the relatively small size of the analysed samples (concrete cores of 50 mm diameter and slices of 7 mm thickness in average). Variation in results might also originate from the number and size of aggregates within the tested sample [9].

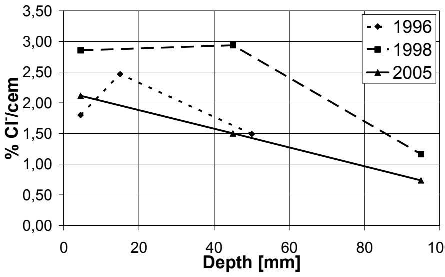

Figure 4: water soluble chloride content location A - non-treated - above tidal zone (1996-1998-2005);

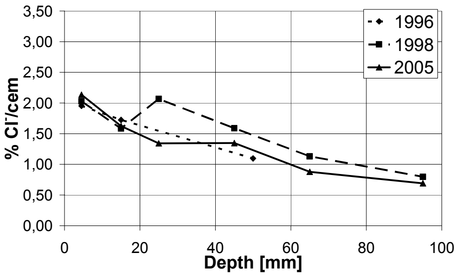

Figure 5: water soluble chloride content location A - non-treated - in tidal zone (1996-1998-2005);

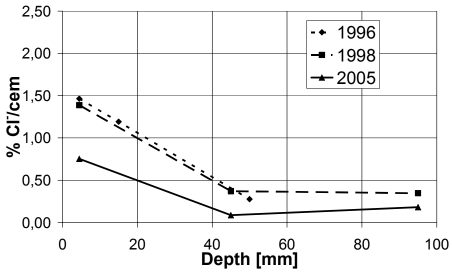

Figure 6: water soluble chloride content Location B-treated with alkyltriethoxysilane above tidal zone (1996-1998-2005);

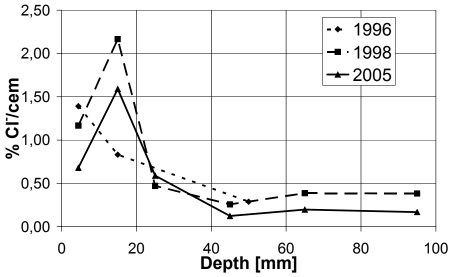

Figure 7: water soluble chloride content Location B-treated with alkyltriethoxysilane in tidal zone (1996-1998-2005);

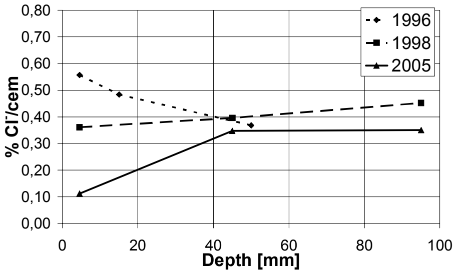

Figure 8: water soluble chloride content - Location C - treated with alkyltriethoxysilane - on top of quay-wall (1996-1998-2005);

In general, the following conclusions can be drawn:

- The largest data scatter corresponds to samples located above the tidal zone. In the tidal zone, the scatter is significantly smaller. This can be due to the higher level of uncertainty related to the exposure conditions above the tidal zone (algae, splash water, increased carbonation depth, salt accumulation, etc.);
- The water soluble chloride concentration in the non-treated area (A) of the tidal zone remains at high levels. The current values vary from 2.2%Cl^-/cem (at the surface) to 0.90%Cl^-/cem (at a depth of 95 mm). The absence of an effective barrier combined with a relatively high porosity (15.6-16.2 vol% [3]) allowed the chlorides to penetrate deeply into the concrete;
- A deep penetration of the hydrophobic agent is crucial to obtain an optimal chloride penetration barrier. The quality of the concrete is more or less equal (except for the concretes variability one can expect from on site applications). The chloride concentrations at treated locations are significantly lower as compared to the respective non-treated locations. When the barrier effect obtained from the water repellent agent is accounted for, significantly lower diffusion coefficients are obtained, see Section 3 and Table 3;
- The corresponding water soluble chloride concentration in the treated area (B) of the tidal zone remains significantly lower. The values vary from 1.20%Cl^-/cem (at the surface) to 0.30%Cl^-/cem (at a depth of 95 mm). The initial chloride content of the concrete is assumed to be C_0=0.03%Cl^-. Since the initial chloride concentration at the moment of construction was not available, this value corresponds to an averaged obtained at a deep location in 1996;
- The chloride attack on top of the quay-wall, i.e., removed from direct exposition but in contact with marine air, is significantly lower;
- Interesting is the increase in chloride ions concentration found at a depth of 15 mm in the treated area (B) of the tidal zone (see Fig. 7). In 1996, after 3 years in service, this was not observed. Subsequently, both in 1998 and in 2005, to a similar extent, a peak in the water and acid soluble chloride concentration was noticed at this depth [9]. The value of the chloride concentration at the peak for the treated area is in the same order of magnitude as the chloride concentration at the surface of the corresponding non-treated areas. In the non-treated areas, this buffering or storage of chloride concentrations in the tidal zone is not present (see Fig. 5). Nevertheless, this peak value at 15 mm beyond the surface does not affect the overall chloride concentration profile at further distances from the surface. At depths greater than 25 mm, chloride concentrations correspond to the initial profiles from 1996.

3 Service life prediction – Random Diffusion Coefficient

Based on the measured material properties and chloride profiles, a service life prediction can be calculated using a time dependent reliability analysis [10-11]. The reliability analysis used is applicable to the durability limit state function of concrete deterioration associated with steel corrosion initiated by the action of chloride ions that reads:

$$g(D) = C_T - C(D, x, t) \tag{1}$$

where C_T is the threshold chloride concentration and $C(D,x,t)$ is the chloride concentration at a distance x from the exposed surface at time t. 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. To account for the uncertainties involved, the diffusion coefficient is taken a lognormal distributed random variable. Its parameters, presented in Table 3, are obtained from the on-site data. For further details, assumptions, and outlined equations the reader is referred elsewhere [10-11].

The predicted service life reflects exceeding of the threshold chloride concentration C_T ,indicated in Table 3, with a target failure probability that equals $P_{f,T}$=0.5, 0.15 and 0.071 (or representative target reliability index: β_T=0.0, 1.0, and 1.5, in which $P_{f,T}=\Phi(-\beta_T)$, with $\Phi()$ the cumulative standard normal distribution function) at a depth of x = 12cm from the concrete exposure surface and starting from the initial exposure in 1993. Several target values for the failure probability were processed covering a range of target values proposed for the durability limit state function. The mid value equals the target failure probability for the serviceability limit state according to ISO2394 [12]. The main concrete reinforcement bars are located at this depth from the exposed surface. Of course, even after this period the structure will not collapse. The predicted service life represents the probability of chloride ions reaching the reinforcement bars at a concentration of 0.7% Cl^-/cem and has to be interpreted as the possible start of the corrosion process or the end of the initiation phase of the concrete deterioration process.

Table 3: Diffusion coefficient D – parameters of lognormal distribution and predicted service life after 5 and 12 years of exposure respectively

Location	μ(D) [cm^2/s]x10^{-8}	σ(D) [cm^2/s]x10^{-8}	Service life [y] C_T= 0.7 % Cl^-/cem		
			$P_{f,T}$=0.5 β_T=0.0	$P_{f,T}$=0.15 β_T=1.0	$P_{f,T}$=0.07 β_T= 1.5
A(non-treated)	9.58	10.55	16.5	7	5
B(treated)	1.61	2.49	107	35	22
C(treated-on top of quay-wall)	2.13	3.46	91	29	18

4 Conclusions

An in-service test program and a service life prediction method based on a time-dependent reliability method are presented. The in-service test program was executed after 3, 5 and 12 years of in-service exposure. The results offer an important long-term data-set of experimental values including on-site chloride contamination of a reinforced concrete structure in a marine environment. The paper contributes to the concept that concrete durability can be increased by means of a preventive in-depth impregnation with an hydrophobising agent to protect it from chloride penetration. Based on the long-term on-site data for the chloride content in the reinforced concrete structures, an objective judgment of the effectiveness could be established. The comparative chloride profiles of a treated and non-treated location demonstrate the effectiveness of the highly concentrated solvent-free alkyltriethoxysilane system as a water repellent agent. The laboratory tests could confirm a penetration depth of the water repellent up to 8 mm with a mean value of 3.5 mm. 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 and quantifies the positive impact of this preventive protection method.

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