

Durability of hydrophobic agents applied in a marine environment

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Abstract

This paper deals with the quay-wall of the new container terminal at Zeebrugge Harbor, Belgium, which is 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 judge the in service effectiveness of the water repellent treatment, three subsequent on-site surveys have been conducted in 1996, 1998, and 2005. The obtained data are used to feed the deterioration models related to the chloride ingress into the structure and to the increase of 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 long-term 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, hydrophobation, water repellent, durability, corrosion

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

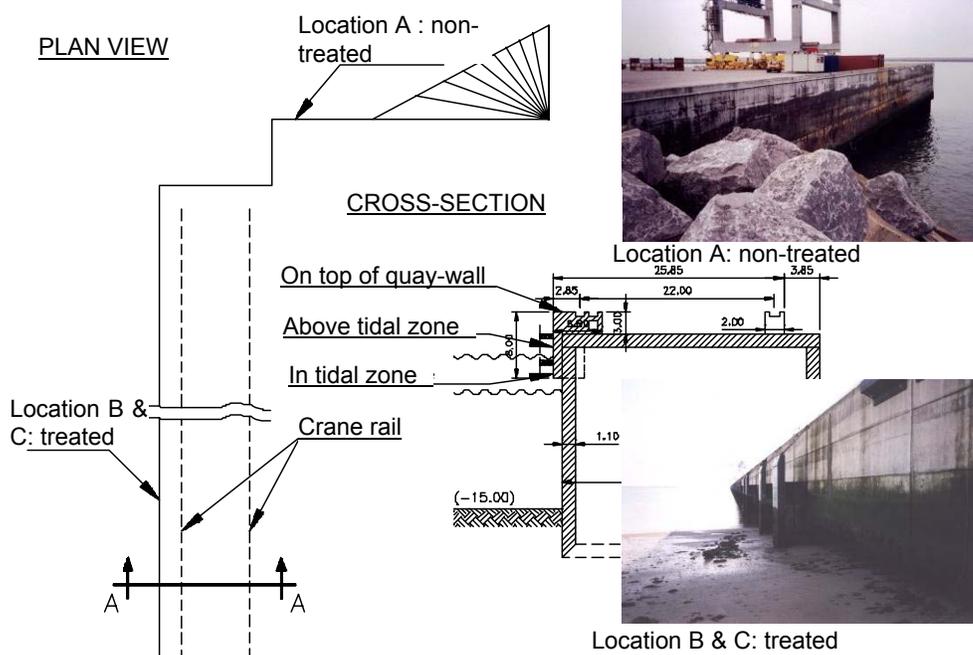


Figure 1: Plan view and cross section of the quay-wall at Zeebrugge Harbor

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 down reinforced cells (caissons). For practical reasons and ease of application it was decided to apply a hydrophobic product with highly concentrated solvent-free compounds based on isobutyltriethoxysilane 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 demolding, prefacing the surface drying of the concrete as well as the eventual initial penetration of salt water;
- a second application was executed 7 days after demolding in order to obtain a deep penetration into the concrete.

The waterproofing was applied by means of airless spraying at low pressures, using a plunger pump. The consumption was determined to be 0.35 litres per m² (300 g/m²) which coincided very well with the preliminary tests on concrete cubes prepared on the construction-site in the laboratory.

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 on-site exposure respectively [3]. Based on these surveys the mid-long term effectiveness could be demonstrated [4-5]. Also, the deep penetration was determined from 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 on-site exposure [7]. Goal of this on-site survey was to update the progress of chloride penetration into the concrete caused by the salty sea-water 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)
- 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 on a long term. Therefore, the values obtained after 12 years of on-site exposure are compared with the data from former on-site surveys.

2 Test campaign

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

- the penetration depth of the hydrophobic agent is determined based on a visual interpretation, by wetting a fresh cracked surface
- the carbonation depth is measured before the cores are sawn into slices on the site directly after drilling as well as in the laboratory the day after drilling for comparison

- after cutting into slices water soluble and acid soluble chloride contents were measured at several depths (figure 2) to determine a chloride penetration profile at different locations

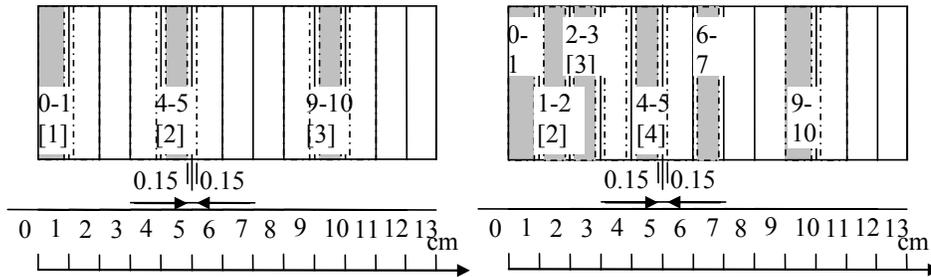


Figure 2: Determining the chloride content at 3 different depths (left) or at 6 different depths (right) from the drilled cores (depth equal to zero equals the outside surface)

2.1 Determination of the impregnation depth

In 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 surface slice of the concrete cores. These slices had an overall thickness from 7 till 9 mm which was sufficient to determine the penetration depth by visual inspection in all cases. In general, the interface between non-hydrophobic and hydrophobic zone was clearly visible, as illustrated in figure 3. Absorption in the non-hydrophobic part gave a darkening of the surface. The values for the impregnation depth varied between 1 and 6 mm, its mean value equaled 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 in 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 hydrophobizing silane system

Location	Visually determined penetration depth [mm]		Concentration alkyltrialkoxysilane [%w/cem] in dependence on penetration depth				
	2005	1998	0mm	2mm	4mm	6mm	8mm [6]
B : above tidal zone	4-6 mm	2-6	1998 [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				

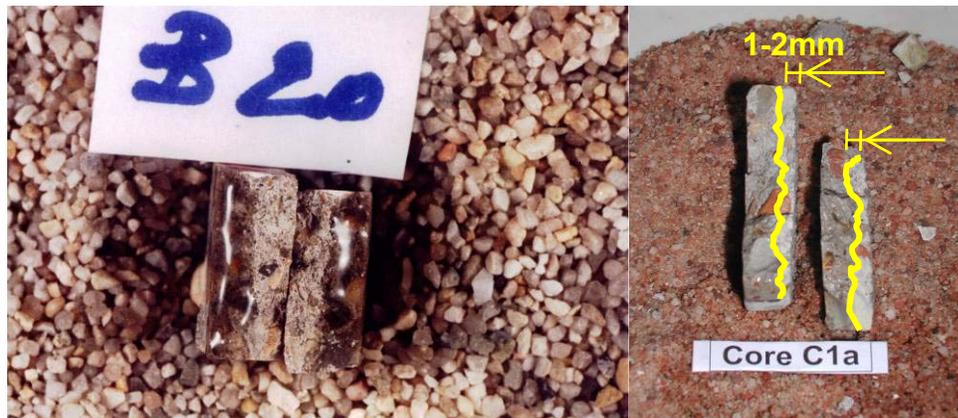


Figure 3: Example of hydrophobic action by means of visual inspection by wetting a fresh cracked surface (slice thickness equals 7 mm) – core B2 (left: 1998) and core C1 (right: 2005)

2.2 Carbonation depth

The carbonation depths were determined by treating the freshly sawn surfaces with a phenolphthaleine 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 compared to the former campaign in April 1998 [7]. Comparing the different locations, it seems clear that the diffusion of CO₂ into the concrete is enhanced causing carbonation since the entrance of water is prevented by means of the hydrophobic agent.

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 Water soluble and acid soluble chloride content – 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 and both types of chloride content were determined at several depths on slices of an average thickness of 7 mm (see figure 3). The chloride contents were determined by means of wet chemical analysis, according to the Belgian Standard NBN B15-250 (1990) [8]. The chloride content, obtained by wet chemical analysis, equals the amount of free chlorides and a great deal of the chlorides bound under the form of salt of Friedel (C₃A.CaCl.10H₂O) which is dissolved in water during extraction. Since the water soluble chlorides represent the chloride ions endangering the steel to corrode, these are reported here solely. 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 3 comparative chemical analyses.

With respect to the presented chloride penetration profiles, some remarks have to be made regarding the accuracy of the experimental results. The data are subject to scatter due to the heterogeneous composition of concrete - aggregates and cement paste as well as the relatively small size of the samples analysed (cores with diameter of 50 mm and slices of concrete with an average thickness of 7 mm). A variation in results might originate from the number and size of aggregates within the tested sample [9].

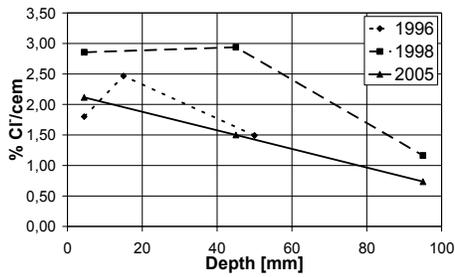


Figure 4: water soluble chloride content - location A - non-treated - above tidal zone (1996-1998-2005);

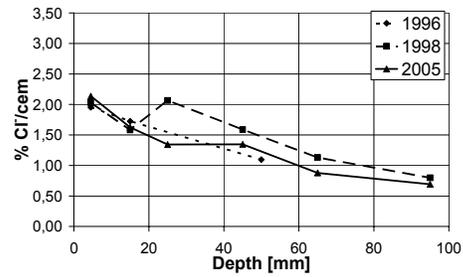


Figure 5: water soluble chloride content - location A - non-treated - in tidal zone (1996-1998-2005);

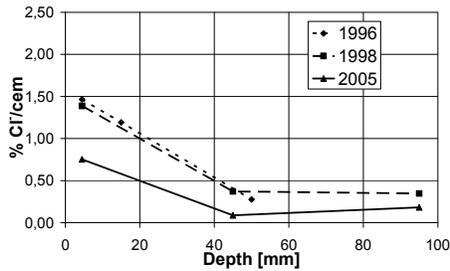


Figure 6: water soluble chloride content Location B-treated with alkyltriethoxysilane - above tidal zone (1996-1998-2005);

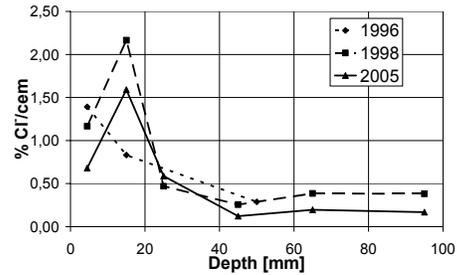


Figure 7: water soluble chloride content Location B-treated with alkyltriethoxysilane in tidal zone (1996-1998-2005);

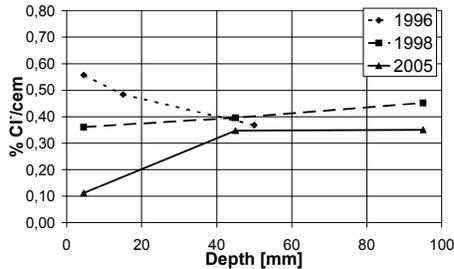


Figure 8: water soluble chloride content - Location C - treated with alkyltriethoxysilane - on top of quay-wall (1996-1998-2005);

In general, the following conclusions can be drawn:

- the scatter is largest for the data of chloride concentration 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,...);

- the water soluble chloride concentration in the non-treated area (A) in the tidal zone remain within the same 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 very deep 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 of its variability one can expect from on site applications). The chloride concentrations at treated locations are significantly lower compared to the respective non-treated locations. When the additional barrier obtained by means of the water repellent agent is accounted for, this results in a significant lower diffusion coefficients, see paragraph 3 and Table 3;
- the corresponding water soluble chloride concentration in the treated area (B) in the tidal zone remain 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 is an average value obtained in 1996 at increased depth;
- the chloride attack on top of the quay-wall, due to marine air and further removed from direct exposition, prove to be significantly lower;
- Surprisingly, however, is the apparent storage of chloride ions which is found at the treated location (B) in the tidal zone at a depth of 15 mm, Figure 7. In 1996 - after 3 years in service - this was not observed. Subsequently, in 1998 and again to a similar extent in 2005, a peak in the water and acid soluble chloride concentration was noticed around 15 mm depth (figure 7) [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 figure 5). Nevertheless, this peak value at 15 mm beyond the surface does not affect the overall chloride concentration profile at larger depth from the surface. From a depth of on 25 mm, chloride concentrations are obtained that correspond with the initial profiles dating from 1996, without the intermediate peak-value, see Figure 7.

3 Service life prediction – Random Diffusion Coefficient

Based on the measured material properties and chloride profiles, 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 the durability limit state function of concrete deterioration associated with steel corrosion initiated by the action of chloride ions that reads:

$$g(D) = C_T - C(D, x, t) \quad (1)$$

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 for which the parameters outlined 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 value C_T with a target failure probability that equals $P_{f,T}=0.5, 0.15$ and 0.071 (or representative target reliability index: $\beta_T=0.0, 1.0,$ and $1.5,$ in which $P_{f,T}=\Phi(-\beta_T)$, with $\Phi()$ the cumulative standard normal distribution function) at a depth of $x = 12\text{cm}$ from the concrete exposure surface starting from the initial exposure at completion of the structure 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 after this period the structure will not collapse. The predicted service life represents the probability for the chloride ions to reach the reinforcement bars with a sufficient concentration of $0.7\%\text{Cl}^-/\text{cem}$ and has to be interpreted as the possible start of the corrosion process or the end of the initiation period 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	$\mu(D)$ [cm ² /s]x10 ⁻⁸	$\sigma(D)$ [cm ² /s]x10 ⁻⁸	Service life [y] $C_T= 0.7 \%$ Cl ⁻ /cem		
			$P_{f,T}=0.5$ $\beta_T=0.0$	$P_{f,T}=0.15$ $\beta_T=1.0$	$P_{f,T}=0.07$ $\beta_T= 1.5$
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, executed after 3, 5 and 12 years of in-service exposure, results in an important long-term data-set of experimental values on on-site chloride contamination of a reinforced concrete structure in a marine environment. This paper contributes to the idea of increasing the durability of concrete by means of a preventive hydrophobic treatment against chloride ingress. Based on long-term on-site data of 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 system based on alkyltriethoxysilane as a water-repellent agent. From the laboratory tests a deep penetration could be observed. When a second treatment is performed after 7 days, a penetration depth of at least 8 mm was reached. When using a visual inspection method, the penetration depth at the cores drilled showed a mean value of 3.5 mm. In case of inspection via pyrolysis GC significant alkylpolysiloxane concentrations were detected again in 8 mm depth. 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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