

Chloride penetration in RC-structures in marine environment – Long term assessment of a preventive hydrophobic treatment

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Abstract

Chloride ingress is one of the main causes of corrosion of the reinforcement in concrete structures, certainly for structures that are highly exposed to chlorides, such as off-shore or on-shore constructions in marine environment. This paper deals with the quay-wall of the new container terminal at Zeebrugge Harbor, Belgium, which is protected against chloride ingress by means of a water repellent agent immediately after construction in 1993 using an alkyltriethoxysilane, pre-evaluated in a preliminary research program. To judge the in site effectiveness of the hydrophobic agent as a water repellent treatment, three subsequent in site surveys have been conducted in 1996, 1998 and recently in 2005. Based on the cores drilled, the chloride profiles are determined as a function of time, both in a non-treated and treated location. The results are presented and discussed. Because of the long-term data sequence, the long-term effectiveness of the treatment can be assessed in an objective way.

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1. Introduction

Chloride ingress due to capillary suction or diffusion is one of the main causes of corrosion of the reinforcement in all concrete structures. A short overview of the durability problem of concrete civil engineering structures in general and in marine environment in particular is given first.

The focus of the paper is on the case study of the quay-wall of the new container terminal at Zeebrugge Harbor, Belgium, that has been constructed in 1993 and was protected against chloride ingress by means of a water repellent agent immediately after construction in 1993. This type of structure is subjected to chloride ingress, not only

below the sea-water level, but also in and above the tidal zone, as well as on top of the quay-wall. The effectiveness of water repellent agents is being studied in the Reyntjens Laboratory of KULeuven. Based on comparative experimental results, it was decided in 1993 to apply Protectosil[®] BH N (former Dynasylan[®] BHN: alkyltriethoxysilane) from Degussa AG on the quay-wall of the new container terminal at Zeebrugge Harbor, Belgium. The production, application and working mechanisms of hydrophobic agents are discussed as well as the laboratory comparative results on the effectiveness of different types of hydrophobic agents.

In order to judge the in site effectiveness of the hydrophobic agent as a water repellent treatment, three subsequent in site surveys have been conducted in 1996, 1998 and recently in 2005, respectively after 3, 5 and 12 years of exposure in the real marine environment of the Belgian North Sea Coast. During each test campaign cores are drilled at different locations and in the treated and in the non-treated zones. From these cores, chloride profiles are

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determined. This allows comparison of the effectiveness of the hydrophobic agent at a certain moment in time and at different location.

The obtained data are used to model the chloride ingress into the structure, for which Ficks' diffusion law is used. In order to account for the scatter in the data, a probabilistic analysis method is applied. The methodology allows for estimating the remaining service life of the structure, both for the treated and non-treated location. The analysis method and results are presented.

2. Durability of reinforced concrete in marine environment

The most frequently occurring deterioration causes of concrete civil engineering structures can be classified in the five categories listed below [1]. It often happens that different causes appear at the same time, are located at different places or amplify each other: (1) damage by external impact on the structure in accidents; (2) damage caused by moisture and water, due to bad functioning of water drains or by inappropriate concept; (3) carbonation damage; (4) corrosion of steel reinforcements induced by chlorides (pitting corrosion); and (5) damage caused by alkali-aggregate reaction (AAR).

Reinforced concrete durability is determined by its resistance against various chemical and physical processes. In normal concrete the reinforcement stays in an alkaline environment with a pH-value of 12.5–13 and under these conditions a dense and well adhering protective patina is formed on the reinforcement surface. This layer with a thickness of approximately 10 nm prevents the reinforcement from corrosion [2,3]. Under the influence of carbon dioxide (CO_2) from the air, the carbonation process occurs. The free lime in the concrete cement paste is bound, and the alkalinity is lost. The pH of the concrete drops to values from 8.5 to 9. When the carbonation depth equals the concrete cover depth, the reinforcement can start to corrode.

For corrosion to happen, the presence of moisture and the ingress of oxygen from the air is needed. Concrete exposed to the outside climate contains enough moisture to keep the corrosion process running and the concrete cover allows the penetration of a sufficient amount of oxygen. Of course, the less permeable and the thicker the concrete cover, the longer will be the time needed for corrosion to appear, and hence, the longer will be the service life of the reinforced concrete structure concerned.

The chlorides in the concrete either come from the components of the fresh mix (water, sand, aggregates, additives), or from external contamination agents (marine environment, de-icing salts). The chlorides, present in the mix, react in different ways [4]: a part ($\approx 5\%$) forms insoluble salts or is locked in the pores of the silicates that are insoluble in water; a part (≈ 85 till 90%) forms soluble salts (Salt of Friedel: $\text{C}_3\text{A}\cdot\text{CaCl}\cdot 10\text{H}_2\text{O}$) and a part ($\approx 5\%$) can be found in the concrete as free chlorides, in solution, or easily soluble by adding water.

The chlorides coming from external contamination agents after the hardening of the concrete, react very little with the solid phase of the concrete, and can be found in the concrete as free chlorides. The water soluble salts (Salt of Friedel) act as a stock of free chlorides. In the presence of these salts, the water in the pores will enrich itself with chlorides until a final concentration is reached that equals the product of solubility. The chlorides that stand for the corrosion risk of the reinforced concrete structure are the chlorides in the pore water (the free chlorides) and a part of the soluble chlorides (Salt of Friedel). At the same time it is a fact that the risk for rust, with a given amount of chlorides in the pore water, will be much higher for a carbonated concrete structure. When aggressive products, like chloride ions, are present in the concrete, the corrosion also takes place in the above-mentioned high alkaline environment. Aggressive elements cause fast and localized corrosion, called pitting corrosion.

The most important sources of chlorides for marine constructions are de-icing salts and the contact with marine air and splash-water. The adding of calcium chloride or other chloride containing compounds as a hardening accelerator means a supplementary chloride source for the concrete.

For constructions in a marine environment or for constructions attacked by de-icing salts, the chlorides will penetrate through the concrete cover in a relatively short time, and when they reach the steel reinforcement surface, the corrosion process can start. Depending on the amount of chlorides, the corrosion process can take place in an alkaline environment. A subsequent phase is the spalling-off of the concrete cover due to the expansive corrosion reaction, which leads to the full exposition of parts of the reinforcement rods to the aggressive environment. In most cases the concrete will give enough warnings before endangering the structure. In pre-stressed concrete this is generally not the case: the pre-stressing cables or strands will break without previous visual damage and warning. In the neighborhood of cracks and fissures the corrosion process is faster because of the easier access of contaminants and because of the reinforcements residing in a low alkaline environment.

The reaction of alkalis with reactive aggregates, also called AAR, is on the contrary of the above-mentioned processes, not a surface reaction [5]. The process happens in the concrete mass. The alkali Na and K, which are present in the cement in the form of their oxides, react with the reactive components of the aggregates if the alkali content exceeds a certain threshold. The reaction produces an alkali-silica gel. By uptake of water this gel swells and causes expansive forces which can destroy the concrete from inside. The degree of swelling depends on many factors, but especially on the moisture content of the concrete. Tests have shown that it is possible to obtain a stable situation of the concrete, even at alkali contents above the threshold, if the moisture content can be kept low enough [5].

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