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# **Chloride Penetration into Water Repellent Concrete Exposed to Sea Water in the Tidal Zone**

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### **Abstract**

Cubes have been prepared with two types of concrete. Three different types of water repellent agents have been selected to be applied on moulded surfaces of part of the concrete cubes. After polymerisation the concrete cubes have been exposed to sea water in a tidal exposure site. The chloride profiles, which have developed in the exposed concrete cubes after an exposure period of 45 days have been determined by means of stepwise milling thin layers of concrete, starting from the surface. The chloride content has been determined in the obtained milling powder by ion-chromatography. The obtained chloride profiles differ in a characteristic way from profiles obtained by continuous laboratory testing. Hence results from laboratory tests can not be used directly for predictions of the service life of reinforced concrete structures. It is necessary to study the underlying migration mechanisms in detail. Experimental data for a realistic life-cycle assessment can be provided only then.

### 1 Introduction

If the surface of concrete structures is exposed to salt water from de-icing salts or to sea water, chloride can penetrate deep into the porous structure in a comparatively short time. This migration process is one of the most important mechanisms of deterioration of reinforced concrete structures worldwide. Both capillary suction and ion diffusion in the pore liquid contribute to this migration process. It is well known by now that water repellent treatment of cement-based materials prevents capillary suction and capillary condensation [1-3]. As a consequence the usual transport mechanisms of chloride in concrete are eliminated by this surface technology. If one succeeds to impregnate a sufficiently thick surface layer of concrete (deep impregnation) this surface technology may be considered to be an efficient chloride barrier for protection of concrete in aggressive environment [4]. Details of the establishment of a chloride barrier and requirements for quality control are described in a recently published preliminary recommendation [5].

So far numerous tests have been run to study the ingress of chloride when the surface is in permanent contact with salt solution. These tests are carried out under well defined laboratory conditions. In parallel observations of chloride profiles in real structures exposed to chloride containing water have been made. In this latter case exposure conditions are more realistic but not easy to describe and results are not ready for generalization.

Along the sea shore at Qingdao, China, a natural sea water exposure site has been arranged. On this protected site concrete specimens can be placed on a height which corresponds to the average sea level between high tide and low tide. This means that during half of each tidal cycle the concrete specimens are under water and the other half they are in air. The specimens will absorb water by capillary suction cyclically for about six hours and then they will loose water again by drying to the atmosphere for another six hours.

In this contribution experiments shall be described to determine the development of chloride profiles in water repellent and untreated concrete. Results shall be compared with measurements on identical concrete but in continuous contact with saline water. Cyclic exposure is usually considered to be more aggressive than continuous exposure. Can this be verified experimentally? One additional major aim of this contribution is to check if experimental results obtained by continuous contact with saline water can be used for a realistic estimation of service life of reinforced concrete structures exposed to tidal sea water.

# 2 Experimental

# 2.1 Preparation of concrete samples

Two types of concrete have been prepared for these tests. One has a W/C of 0.4 and the other of 0.6. The composition of the two types of concrete is indicated in Table 1. Crushed aggregates with a maximum diameter of 25 mm and river sand with a maximum diameter of 5 mm have been used. Concrete was made with a Chinese ordinary Portland cement, similar to CEM I. Concrete cubes with an edge length of 100 mm have been cast. After two days they were de-moulded and stored in a humid chamber at a temperature of approximately 20 °C and relative humidity close to 100 % for 14 days. Then they were stored in laboratory climate with approximately 20 °C but about 50 % relative humidity. At an age of 56 days one surface of part of the cubes has been treated with liquid silane, silane cream or silane gel. The cubes were further stored in the laboratory for two weeks before both treated and untreated cubes have been placed in the tidal exposure site.

## 2.2 Tidal exposure site

In order to be able to expose concrete samples to natural sea water attack under controlled conditions a tidal exposure site has been arranged at the sea shore close to Qingdao, China. The rocky slope is oriented towards south facing the Chinese sea. A place has been selected on the rocks, the height of which corresponds to the average sea level between ebb and flood. The concrete cubes have been stored in a cage to protect them from being washed away by strong waves. The site is controlled and easily accessible and therefore samples can be taken from the site to the laboratory for analysis at any time without difficulties. By the way, this site is also suitable for testing full size reinforced concrete members.

After 45 days the first samples have been taken back to the laboratory for analysis. Results will be presented in this contribution. Other samples of this series remained on the site for later analysis.

**Table 1:** Composition of the two types of concrete. Specific mass is indicated in kg/m<sup>3</sup> throughout

	Cement	Gravel	Sand	Water	W/C
Concrete A	380	1269	579	152	0.4
Concrete B	300	1210	710	180	0.6

# 2.3 Determination of chloride profiles

After a predetermined exposure time cubes have been taken back to the laboratory. From the untreated and water repellent concrete cubes 1 mm thick slices have been milled by means of a specially developed milling cutter successively. The powder obtained in this way has been collected in small plastic bags and later the chloride content has been determined by means of ion-chromatography. In the same way silicon resin profiles can be determined by means of FT-IR spectroscopy [6].

#### 3 Results and discussion

The chloride profiles which had developed in concrete with W/C = 0.4 after 45 days of exposure in the tidal exposure site in untreated and water repellent concrete are shown in Fig. 1. In this case a minimum amount of water repellent agent has been applied. The concrete surface has been in contact with liquid silane for 5 minutes only and  $100 \text{ g/m}^2$  of silane cream and silane gel have been applied with a brush.

As can be seen from Fig.1 chloride has penetrated deep into the concrete cubes after exposure for 45 days. At a distance of 20 mm from the surface

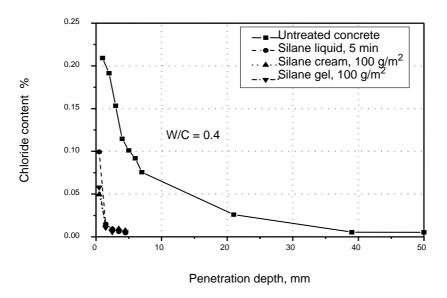


Figure 1: Chloride profiles as determined from concrete cubes with W/C = 0.4 after exposure in the tidal sea exposure site for 45 days

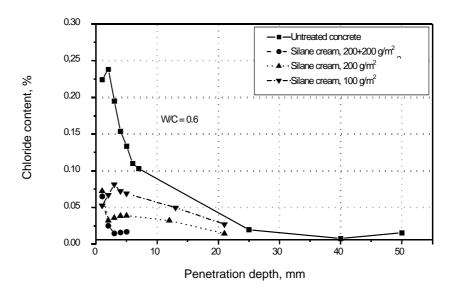


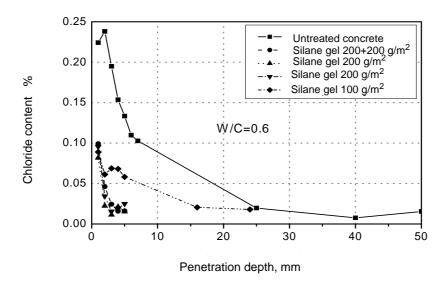
Figure 2: Chloride profiles of untreated and water repellent concrete with W/C = 0.6, treated with different amounts of silane cream, after exposure to sea water in the tidal zone for 45 days

chloride can still be detected. The small amount of water repellent agents applied was enough to reduce the penetration depth considerably. It will be interesting to see if this chloride barrier still works at longer exposure durations.

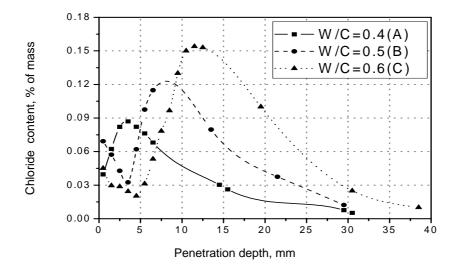
In Fig. 2 the chloride profiles as measured in concrete cubes with W/C = 0.6 are shown. The profile of untreated concrete is plotted together with the profiles of concrete cubes which had been treated with different amount of silane cream. When 200 g/m² of silane cream are applied and one week later the same amount again, that means if 400 g/m² are applied altogether, an efficient chloride barrier has been built up. But if 100 g/m² or 200 g/m² are applied just once chloride penetrates significantly already after 45 days.

On other cubes one moulded surface of concrete has been treated by coating it with different amounts of silane gel. Results after exposure to sea water for 45 days are shown in Fig. 3. As can be seen, in this case application of  $100 \, \text{g/m}^2$  of silane gel has definitely not been sufficient, chloride starts to penetrate at an early stage. If more silane gel is applied at least for 45 days a chloride barrier has been built up.

For comparison the chloride profiles which have been measured on cubes made of similar type of concrete but exposed to saline water in the laboratory continuously for 28 days are shown in Fig. 4 [7]. First of all it is remark-



**Figure 3:** Chloride profiles of untreated and water repellent concrete with W/C = 0.6, treated with different amounts of silane gel, after exposure to sea water in the tidal zone for 45 days



**Figure 4:** Chloride profiles as observed in untreated concrete samples with different W/C after continuous contact of the surface with saline water for 28 days [7]

able that the characteristic shape of the profile after exposure to sea water continuously and the corresponding profile after exposure to sea water in the tidal zone is quite different. In the case of direct and continuous contact with salt water a marked maximum is observed at a given penetration depth. In the case of exposure to natural sea water in the tidal zone, however, the highest chloride concentration is measured close to the surface followed by a continuous decrease with increasing distance from the surface.

Second, the maximum chloride content in samples exposed to sea water in the tidal zone is much higher than the maximum value as measured on samples exposed continuously to sea water (see Figs. 1,2, and 4). During continuous suction for 28 days chloride has penetrated deeper as compared to the samples exposed in the tidal zone.

These obvious differences have to be studied in more detail. The origin of the difference will have to be elucidated by comparison of experimental data with numerical models. We can apply experimental results from laboratory testing to arbitrary exposure conditions only, if we understand the time-dependent development of the resulting profiles.

If we consider that in practice usually large surfaces have to be impregnated and if we take the inevitable local variability of the substrate and variations of the surface treatment into consideration, a reliable and durable chloride barrier can be built up only, if it can be ascertained that even the local minimum penetration depth is still sufficient. The corresponding extreme value contributions have to be determined and considered. In order to indicate justified critical safe minimum values for the average penetration depth more experimental data and a rigorous probabilistic assessment are needed.

## 4 Conclusions

- When concrete is in continuous contact with saline water the chloride profile shows a marked maximum at a certain penetration depth. Both the amount of chloride, which is taken up, and the penetration depth depend on the quality of concrete and the type of exposure to saline water.
- The characteristic chloride profile in concrete depends strongly on the type of exposure. Experimental data from laboratory testing can not be used directly if the chloride penetration under arbitrary exposure conditions is to be predicted.
- The different shape of the chloride profiles can be understood only, if its physical origin can be explained by means of numerical modelling.

- More experimental data and a thorough probabilistic assessment are needed in order to fix safe and justified critical minimum quantities of water repellent agents which have to be applied by surface treatment, if a reliable and durable chloride barrier is to be established.
- The effective penetration depth of the water repellent agent is the decisive parameter to be checked in context of quality control.

# 5 Acknowledgement

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