On Surface Impregnation of Chloride Contaminated Cement based Materials

T. Zhao¹, G. Zhu¹, F. H. Wittmann^{1,2}, and W. Li³ ¹Qingdao Technological University, Qingdao, China ²Aedificat Institute Freiburg, Germany ³Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China

Abstract

It has been shown some time ago that young and uncontaminated concrete can be surface impregnated by liquid silanes in order to provide a protective barrier against ingress of chloride ions. In practice, existing reinforced concrete structures, which have been in contact with aqueous salt solutions for some time, also need to be protected when the risk for corrosion becomes obvious. In this contribution capillary suction of concrete has been measured. The coefficient of capillary suction is considered to be a reliable measure for the estimation of chloride penetration under given climatic conditions. It could be shown that moderate chloride content allows to apply surface impregnation of silanes successfully as a protective measure and to avoid further chloride ingress. High chloride content and low water-cement ratio make surface impregnation difficult if not impossible. Therefore it is recommended to test the efficiency of application of silane on concrete surfaces of old structures before a protective measure is carried out.

Keywords: surface impregnation, silane, chloride content, moisture content.

1 Introduction

Concrete is a porous material with a wide range of pore sizes. Nano-pores are predominant in the hydration products of cements while compaction pores with a diameter of several millimetres can be observed in structural elements. Concrete just as other similar porous systems has an intense interaction with moisture of its environment. The huge internal surface of the nano-structure absorbs water from the environment even at very low relative humidity. From air with a relative humidity higher than 50 %, liquid water is formed and retained by capillary condensation where the properties of the condensed water are modified. If the surface is in contact with liquid water or with aqueous salt solutions significant quantities of water are absorbed by capillary suction. Under drying conditions the moisture content is reduced again with a marked hysteresis. All changes of moisture content will induce volume changes which are at the origin of crack formation. Durability of a concrete structure depends essentially on this complex interaction between the porous material and its surrounding.

In this contribution capillary suction will be considered in particular. Capillary suction is one specific process of capillarity of porous materials and an efficient mechanism to transport liquid water into the porous space of concrete. Dissolved ions are transported together with the water flow into the material but with some retardation (micro-filter effect) [1, 2]. In case the surface of concrete has been impregnated with liquid silanes, capillary forces are nearly completely suppressed and hence the capillary suction is eliminated. Usually capillary depression is observed, that means water might penetrate the pore space of a water repellent material if under pressure. In practice, driving rain or hydraulic pressure of a water volume on top of a concrete surface are two examples for possible water ingress in water repellent concrete.

It has been shown by a number of authors that deep impregnation of the concrete surfaces with water repellent agents forms an efficient and longlasting barrier with respect to chloride ingress [3-8]. In this way service life of reinforced concrete structures situated in an aggressive environment such as marine climate can be significantly extended.

Most recommendations for design and applications in practice are written for surface impregnation of comparatively young and non-contaminated concrete structures. However, there are many concrete structures, all over the world, which have been exposed to chloride containing water for many years, before the risk of corrosion and the associated costs of repair measures and maintenance are realized. Is it possible to make chloride contaminated concrete water repellent by surface impregnation? Can we protect contaminated concrete from further ingress of chlorides? This contribution should help to find answers to these two questions. Results of test series with the major aim to investigate the feasibility of surface impregnation of chloride contaminated concrete will be presented and discussed in this contribution.

2 **Preparation of samples**

Cubes with an edge length of 100 mm have been prepared from four different types of concrete with a water-cement ratio ranging between 0.4 and 0.6 in steel moulds. Crushed granitic aggregates with a maximum diameter of 20 mm and river sand with a maximum diameter of 5 mm and a fineness modulus of 2.9, both from the area around Qingdao, China, have been used. Ordinary Portland cement with grade 32.5 has been selected for this test series. 20 % of the Portland cement has been replaced by a local fly ash in one mix (Type D). A super-plasticizer (SP) of the naphthalene type has been added to all mixes to reach good workability. The exact composition of the four types of concrete, which have been investigated in this project, is given in Table 1.

Туре	Cement	Sand	Aggregate	Water	SP	Fly ash	Slump(mm)	W/C (W/B)
А	380	579	1269	152	5.7	-	10	0.4
В	320	653	1267	160	4.8	-	22	0.5
С	300	710	1210	180	4.5	-	110	0.6
D	256	653	1267	160	4.8	64	90	0.5

 Table 1:
 Composition of the four types of concrete; related mass is indicated in kg/m³.

All concrete cubes have been kept in steel moulds under wet cloth in the laboratory at room temperature for two days. Then they were demoulded and stored in a humid chamber at a temperature of 20 ± 2 °C and a relative humidity (RH) above 95 %. At an age of 14 days all cubes were cut in halves from top to bottom in the direction of casting. The half cubes were then further stored in the laboratory at 20 ± 2 °C and approximately 50% RH. At an age of 28 days the four smaller surfaces (50 x 100 mm²) of the prisms were sealed with warm paraffin wax. Then the concrete specimens were ready for surface treatment on the moulded of the two free surfaces and for the determination of capillary suction.

3 Chloride profiles

Chloride profiles were established in the concrete specimens after capillary suction of an aqueous 3 % NaCl solution through the moulded surfaces ($100 \times 100 \text{ mm}^2$) for 28 and 90 days. After this exposure, layers with a thickness of 1 mm have been milled off from the surface successively. The gained powder has been suspended in water. The water-soluble chloride content of the powder obtained in this way was determined by means of a calibrated ion selective electrode.

Both reference and contaminated samples were impregnated with a liquid silane (Wacker BS 1701, isooctyltriethoxysilane) by direct contact for one hour. This impregnation technology meets the requirements of recent recommendations for design and application of water repellent agents [9]. In this way deep impregnation of the outer layer of concrete can be achieved through the surface. In practice liquid silane has to be applied in a number of runs (up to 7) or by applying an appropriate amount of silane cream or gel.

4 Capillary suction

Capillary suction has been used in this paper as a measure for the effectiveness of a surface impregnation with a water repellent agent. In order to understand the results and the following discussion, basic equations of capillary suction will be presented. The moulded surfaces of treated and untreated concrete specimens have been put in contact with water. The amount of absorbed water ΔW as function of time t can be reasonably well approximated with the following equation [4-6]:

$$\Delta W = \left[A_o + \frac{A_1 t}{\left(A_2 + t \right)} \right] \sqrt{t} \tag{1}$$

 A_0 , A_1 , and A_2 are constants, which have to be determined by data fitting. The initial coefficient of capillary suction A_i can be described under the assumption that A_1 and A_2 are zero. Then equation (1) becomes the usual equation to describe capillary suction of homogeneous materials:

$$\Delta W(t) = A_i \sqrt{t} \tag{2}$$

with A_i being the initial coefficient of capillary suction $[kg/(m^2 h^{1/2})]$:

$$A_{i} = \Psi \rho_{\sqrt{\frac{r_{eff} \sigma \cos\Theta}{2\eta}}}$$
(3)

and ΔW the related absorbed mass of liquid [kg/m²]. In equation (3) Ψ stands for the water capacity [m³/m³] and ρ for the density of water or the salt solution [kg/m³], while σ represents the surface tension [N/m], Θ the wetting angle and η the viscosity of the absorbed liquid [(N s)/m²]. r_{eff} is an

effective pore radius [m] characterizing the complex pore size distribution of the material under investigation.

For homogenous porous materials with equally distributed moisture content the coefficient of capillary suction A is approximately constant during the contact time (see eq. 2). In concrete, however, there is a marked skin effect [10]; that means the outer layer differs from the bulk material. The porosity is much higher near the surface. Therefore a space dependent coefficient of capillary suction A is introduced in equation (1). At the beginning of the suction process the coefficient of capillary suction is $A = A_0 = A_i$, while at a later stage a lower value is asymptotically reached: $A' = (A_0 - A_1)$.

If a concrete sample is not in hygral equilibrium, there exists a hygral gradient in the material. In this case the penetrating water front meets layers with increasing or decreasing water content on its way. The coefficient of capillary suction decreases, when the water front reaches layers with increasing water content and vice versa. At higher water content the free water capacity Ψ in equation (3) decreases. In addition the effective radius r_{eff} increases. The overall result is a decrease of both the rate of absorption and the amount of absorbed water.

The penetration depth x(t) of water can also be described approximately for many porous materials as function of square root of time:

$$x(t) = B\sqrt{t} \tag{4}$$

When A has been determined, B, the coefficient of initial capillary penetration $[m/s^{1/2}]$, can be obtained by the following equation:

$$B = \frac{A}{\Psi \rho}$$
(5)

In an initial phase, A and B can be replaced by A_i and B_i . We can estimate the penetration depth x(t) in the initial phase by means of equation (4). As soon as the capillary suction function deviates significantly from a straight line, the initial phase comes to an end. The estimation of the penetration depth beyond the initial phase of capillary suction is more complicated.

5 Results and discussion

5.1 Capillary suction of reference and surface impregnated noncontaminated concrete

As a first step the capillary suction of the four types of concrete was determined as function of time. The obtained values serve as reference for the capillary suction of surface impregnated and chloride contaminated specimens. Results are shown in Fig. 1. The measured data have been fitted with equation (1). It is evident that the simple square root of time law (see eq. (2)) is fulfilled in the initial phase of capillary suction only. At a later stage the rate of absorption is slowed down as mentioned above. A_i is the tangent to the initial part of the sorption curve and the obtained values for the four types of concrete are compiled in the second column of Table 1. As expected, capillary suction of untreated specimens, expressed in terms of A_i, increases with increasing water-cement ratio. On concrete D, which was prepared by replacing 20 % of Portland cement by fly ash, a comparatively high capillary suction has been observed. We explain this effect by the slow reaction of fly ash as compared to ordinary Portland cement. Most probably the capillary suction of concrete type D will be reduced at a later stage as hydration continues.



Figure 1: Amount of absorbed water by capillary suction as function of contact time.

Type of	Ai	A _i *, water		
Concrete	untreated	repellent		
A	0.440	0.016		
В	0.700	0.024		
С	0.833	0.020		
D	0.950	0.020		

In Fig. 2 water absorption, as measured on water repellent concrete, is shown. For comparison the data obtained on untreated concrete as shown in Fig. 1 are represented again. It is obvious that deep impregnated water repellent concrete absorbs a small amount of water only. As capillary suction is suppressed in water repellent concrete, we may assume that moisture enters concrete essentially due to water vapour diffusion through the impregnated zone and not due to capillary suction. For reasons of comparison we have determined A_i^* of water repellent concrete as well. The small values obtained are also given in Table 2, in the third column. But we must keep in mind that A_i^* in this case represents in fact vapour permeability and not capillary suction. Then it is of course more realistic to replace eq.(2) by the following expression:

$$\Delta W(t) = \lambda_h \Delta h / \Delta x$$

(6)

In eq.(6) $\Delta W(t)$ stands for the penetrated amount of water vapour per unit surface und unit of time, λ_h stands for the coefficient of water vapour permeability and Δh for the difference of moisture potential over a water repellent layer having a thickness of Δx . With increasing thickness of the water repellent layer, the amount of water, which enters the material by water vapour diffusion, decreases. Behind the water repellent layer, part of the water vapour that entered the sample will be trapped by capillary condensation and the remaining part will further migrate deeper into the material. At the moment we are at the beginning of understanding these complex mechanisms only. As it is vital for the durability of surface impregnated concrete, research in this area is now going on.



Figure 2: Capillary suction of reference samples of the four types of concrete A, B, C, and D (CA0, CB0, CC0, and CD0), and of samples after surface impregnation with liquid silane (CAOL, CBOL, CCOL, and CDOL).

5.2 Capillary suction of chloride contaminated concrete

In order to study the influence of chloride content on the effectiveness of surface impregnation with silane, concrete specimens were put in contact with aqueous 3 % NaCl solution for 28 and 90 days. Chloride profiles after this exposure were determined as described in section 3. Results obtained on the four types of concrete after exposure to salt solution for 28 days are shown in Fig. 3. The penetration depth increases slightly with increasing water-cement ratio. The corresponding chloride profiles as determined in the four types of concrete after exposure to aqueous NaCl solution for 90 days are shown in Fig. 4. The specific shape of the profiles shown in Figures 3 and 4 is an indication that mechanisms other than diffusion are responsible for penetration of chloride into the porous structure of concrete. This is in agreement with earlier findings [4, 5].



Figure 3: Chloride profiles as measured in the four types of concrete A, B, C, and D after contact of the surface with aqueous 3 % NaCl solution for 28 days.

The profiles shown in Figs. 3 and 4 are difficult to interpret in a quantitative way. Probably some chloride migrated out of the concrete during drying before grinding. Further investigations have to elucidate this unsatisfactory situation.



Figure 4: Chloride profiles as measured in all four types of concrete A, B, C, and D after contact of the surface with aqueous 3 % NaCl solution for 90 days.

In the next step capillary suction of chloride-contaminated concrete has been measured. In Fig. 5 results are shown for concrete which has been in contact with aqueous 3 % NaCl solution for 28 days and 90 days. For comparison the results obtained on uncontaminated concrete are shown again. It can be clearly seen, that chloride contamination reduces the coefficient of capillary suction significantly. There are at least two different mechanisms, which are at the origin of this observation. In concrete with high water-cement ratio salt solution is retained in coarse pores during the drying process and therefore less pore space is available for subsequent absorption. The saturated salt solution at 20 °C is in hygral equilibrium with a lower relative humidity (approximately 75 %) as compared to pure water. Partial dissolution of crystallized salt has to be expected. These different mechanisms are to be studied in more detail in the future.



Figure 5: Capillary suction of all four types of concrete A, B, C, and D, untreated (CAO, CBO, CCO, and CDO), after contact with salt solution for 28 days (CA1, CB1, CC1, and CD1), and for 90 days (CA3, CB3, CC3, and CD3)

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5.3 Capillary suction of chloride contaminated concrete after surface impregnation

Concrete samples, salt contaminated as described above, have then been surface impregnated with liquid silane in the same way as described in section 3 for non-contaminated concrete. Results are shown in Fig. 6 and Fig. 7 for concrete, which was in contact with a salt solution for 28 and 90 days, respectively. For comparison capillary suction of uncontaminated specimens is shown again in Fig. 6. The chloride content after 28 days of contact with salt solution has hardly any influence on the effectiveness of surface impregnation.



Figure 6: Capillary suction of the four types of concrete A, B, C, and D in the untreated state (CA0, CB0, CC0, and CD0), after surface impregnation with liquid silane (CA0L, CB0L, CC0L, and CD0L), after contact with salt solution for 28 days (CA1, CB1, CC1, and CD1) and after surface impregnation following chloride contamination (CA1L, CB1L, CC1L, and CD1L).

The capillary suction is practically suppressed to such a degree that we may assume that water vapour can penetrate but no liquid water. This means that dissolved ions cannot be transported into the pore space of chloride contaminated and surface impregnated concrete.

After contact of the concrete surface with the salt solution for 90 days the situation changes in particular for concrete with low water-cement ratio. From Figure 5 we learn that capillary suction of concrete with W/C = 0.4 is reduced to a minimum. We assume that salt crystals block the comparatively small pore space near the surface (see Fig. 4). In this case surface impregnation is not possible any more. At higher W/C values, however, capillary suction can still be observed after the same exposure to salt solution. In this case surface impregnation still reduces capillary



Figure 7: Capillary suction of the four different types of concrete A, B, C, and D after chloride contamination for 90 days, untreated (3) and surface impregnated (3L).

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suction of contaminated concrete significantly although the efficiency of surface impregnation is reduced. There is obviously a critical chloride content, which depends on the water-cement ratio of concrete; if this value is overcome, the material cannot be surface impregnated with liquid silanes anymore.

6 Conclusions

Based on the results shown in this contribution it can be concluded that:

- Moderate salt contamination reduces capillary suction of concrete, different mechanisms are at the origin of the observed reduction. Further research is necessary to elucidate their relative contributions.
- Capillary suction of moderately salt contaminated concrete can be significantly reduced by surface impregnation. That means further ingress of chlorides can be reduced; this corresponds to an extension of service life of already contaminated reinforced concrete structures by surface impregnation.
- Reduction of the equilibrium moisture content in concrete structures after surface impregnation further contributes to an extension of the service life.
- Pore space of concrete with low water-cement ratio can be easily blocked by salt crystals, which grow during drying; in this state concrete cannot be surface impregnated any more.
- In case concrete has been exposed to marine or similar aggressive environment for some time, it is recommended to test the efficiency of surface impregnation with silane, prior to an application of surface impregnation as a protective measure.

Acknowledgement:

The authors of this contribution gratefully acknowledge support of the ongoing project by Natural Science Foundation of Qingdao City (Contract No. 06-2-2-14-jch) and Qingdao Guoxin Corporation Ltd. (Contract No. 20063702001811).

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