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Water Repellent Surface Treatment in Order to Establish an Effective Chloride Barrier

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Abstract

Water repellent treatment can be applied to concrete structures in order to achieve a variety of completely different aims. In this contribution the potential of water repellent treatment to act as an efficient, reliable and durable chloride barrier will be investigated. As capillary suction is a powerful mechanism for transporting dissolved chlorides into the porous structure of concrete the influence of water repellent treatment on water up-take is first studied. Further it is shown that deep impregnation of concrete with silane of at least 5 mm leads to a chloride barrier if the surface of concrete is exposed to 3 % sodium chloride solution. A small amount of silane is sufficient to reduce chloride penetration considerably. But below a critical amount of water repellent agent chloride can penetrate through the impregnated surface layer. Minimum values for the penetration depth of the agent are recommended. Further research is needed, however, in order to provide a solid basis for a comprehensive reliability analysis of water repellent treatment of concrete structures.

1 Introduction

Reinforced concrete structures often are exposed to an aggressive environment. Under these conditions service-life can be limited by penetration of chemical compounds such as CO_2 or chloride through the concrete surface. These compounds may react with the hydration products of Portland cement or destroy the protective layer of reinforcement steel respectively. As a consequence usually expensive repair measures are necessary at an early stage. Chloride may enter the porous structure of concrete either by diffusion or by capillary suction and in most cases by a combination of both transport processes. Capillary suction is most effective if the surface of a structural concrete element is directly exposed to seawater or during a winter period to salt water after application of de-icing salts.

An effective water repellent surface treatment prevents capillary suction nearly completely. In case the penetration depth of the water repellent agent is sufficient chloride penetration may be reduced to a tolerable degree. It has been shown earlier that the application of an integral water repellent mortar can act as a reliable chloride barrier [1]. In another project surface treatment with liquid silane of a quay wall has been applied in order to establish a chloride barrier [2]. Recently a preliminary version of a recommendation for the surface technology of water repellent treatment has been published [3]. In this document requirements (deep impregnation) for an effective chloride barrier are formulated. The revised final version will be available soon.

In the present contribution the capillary suction of four types of concrete has been studied first. Then samples of all four types of concrete have been treated with three different water repellent agents: liquid silane, silane cream, and silane gel. The application technology has been varied in order to obtain different penetration depth of the water repellent agents. One major aim of these investigations has been to provide an experimental basis for the definition of the minimal allowable penetration depth for an efficient and durable chloride barrier.

2 Experimental

2.1 Preparation of concrete specimens

Four types of concrete with different water-cement ratios have been manufactured for the surface treatment with different water repellent agents. Crushed aggregates with a maximum diameter of 25 mm and river sand with a maximum diameter of 5 mm have been used as aggregates. Chinese ordinary Portland cement (similar to Type CEM I) has been selected for this

Table 1: Composition of the four types of concrete. Specific mass is indicated in kg/m^3 throughout

	Cement	Gravel	Sand	Water	W/C	FA	SP
Concrete A	380	1269	579	152	0.4	-	+
Concrete B	320	1267	653	160	0.5	-	-
Concrete C	300	1210	710	180	0.6	-	-
Concrete D	256	1267	653	160	0.5	64	-

project. The exact composition of the different types of concrete is given in Table 1. Concrete A has a low water-cement ratio of 0.4. In this case super plasticizer (SP) has been added to maintain good workability. In concrete D 20 % of the Portland cement has been replaced by fly ash (FA). The real water-cement ratio for concrete D is 0.625 and the water-binder ratio is 0.5. Concrete D has been included in order to study the influence of fly ash on capillary suction.

Concrete cubes with an edge length of 100 mm have been cast from all four mixes. After two days they have been de-moulded and then stored in a humid chamber at a temperature T of 20 ± 3 C and a relative humidity RH of nearly 100 % until an age of 14 days. At this age the concrete cubes have been cut with a diamond saw into two halves from top to bottom. The two halves have then been stored in the laboratory at a temperature of 20 ± 3 C and a relative humidity of approximately 50 % for another 42 days. At an age of 56 days moulded surfaces of the half cubes (100 x 100 mm) have been impregnated with the three types of water repellent agents under investigation. The four smaller surfaces (50 x 100 mm) have been sealed with wax and the cut surface remained untreated.

2.2 Water repellent treatment

The moulded concrete surfaces of the half cubes have been treated with three different water repellent agents. One series has been treated with liquid silane. In this case the concrete surface was put in contact with the liquid silane for selected periods of time. During these periods silane could be absorbed by capillary suction. The amount of silane absorbed has been determined gravimetrically [4]. Some samples have been treated a second time after one week for one hour.

In a second and third series the moulded surfaces of sawn half cubes have been treated with silane-based cream and gel. In [4] a short characterization of the selected cream and gel is given. Different amounts of cream and gel ranging from 100 to 600 g/m^2 have been applied with a brush.

2.3 Determination of capillary suction

Capillary suction of treated and untreated concrete has been measured by a standard method [5]. In this case the untreated and treated surfaces of the half cubes are placed in direct contact with water and the water absorbed by capillary suction is measured by weighing the concrete specimens after different durations of contact (see also [4] and [6]). It has been shown that for concrete the amount of water absorbed by capillary suction is linear if plotted as function of the square root of time for a comparatively long time. From the measured data the coefficient of capillary absorption A can be determined.

2.4 Determination of silicon resin and chloride profiles

Qualitative information on the penetration depth of the water repellent agents can be obtained by spraying a freshly broken surface with tap water. The surface of the water repellent material does not absorb the sprayed water and therefore remains light as compared to the untreated material which darkens remarkably when the surface near pores are getting water filled. From five to ten individual measurements a mean value of the penetration depth has been determined in this way. This simple optical method, however, does not give us any information concerning the quantity of water repellent agent in the porous structure nor does it tell us something about the distribution of the active substance in the surface near zone. Therefore a more sophisticated method has been applied in addition.

From the water repellent treated concrete specimens layers parallel to the initial moulded surface and having a thickness of one mm each have been milled by means of a specially built diamond milling cutter consecutively. The powder obtained from this process was collected in small plastic bags. Later the silicon content of these powder samples has been determined by means of FT-IR spectroscopy. This method has been developed and further refined for this specific application by A. Gerdes [7, 8].

In a similar way powder samples have been milled consecutively from treated and untreated samples starting at the surface of concrete specimens which have been exposed to salt solutions [9]. The chloride content of the powder samples has been determined by means of ion-chromatography [10, 11]. In this way chloride profiles as built up in treated and untreated concrete have been measured directly.

3 Results and Discussion

3.1 Capillary suction of untreated concrete

Water absorption of the four different types of concrete has been measured for a maximum duration of contact of 72 hours. Results obtained on different untreated concrete samples are shown in Fig. 1. Points indicated in Fig. 1 are average values of at least three independent measurements.

A simple equation can be deduced theoretically to describe capillary absorption as function of time as a first approximation. In equation (1) W stands for the amount of water absorbed by capillary suction per unit of contact surface and t for the duration of contact:

$$\Delta W = A\sqrt{t} \tag{1}$$

A is the coefficient of capillary suction. From Fig. 1 it can be seen that equation (1) describes the time dependence of capillary suction of concrete reasonably well within the duration of contact under investigation. The coefficient of capillary suction A characterizes the capillary water uptake by the porous structure of the different types of concrete. Values of A as obtained

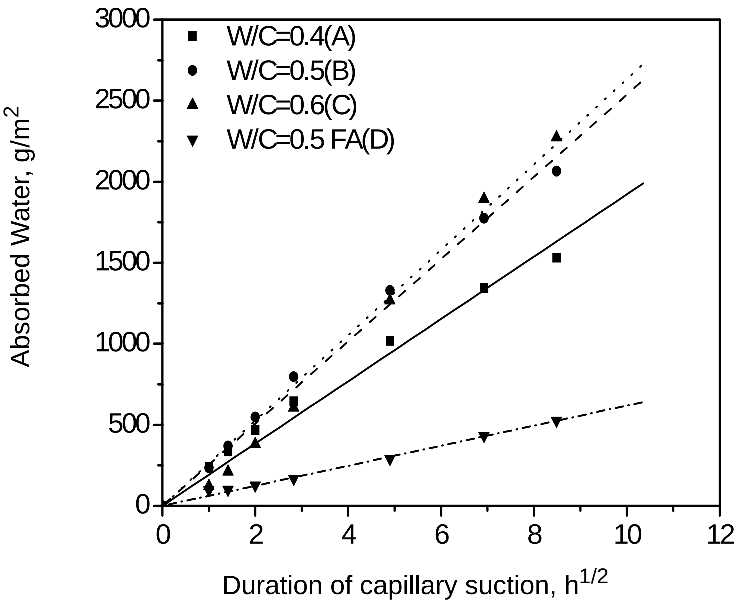

Figure 1: Water up-take by capillary suction of untreated concrete

Table 2: Coefficients of capillary suction A of untreated and A' of treated concrete. Values of A and A' are given in kg/(m^2 $h^{1/2}$)

Type of concrete	W/C	A (untreated)	A'(treated)
Concrete A	0,4	0.194	0.020
Concrete B	0.5	0.254	0.025
Concrete C	0.6	2.261	0.040
Concrete D	0.5	0.062	0.025

from the experimental results by linear regression are compiled in Table 2 and the corresponding linear functions are shown graphically in Fig. 1. It is obvious that the concrete that contains fly ash has a comparatively small coefficient of capillary suction. This observation can be explained by the denser structure of the hardened cement paste that is formed when part of the Portland cement is replaced by smaller particles of fly ash.

3.2 Capillary suction of water repellent concrete

Values A' in Table 2 have been determined on concrete samples after water repellent treatment. The surface of concrete has been treated with liquid silane and with silane-based cream and gel. These values should not be considered to be real coefficients of capillary suction, however. Water uptake of water repellent concrete is due to water vapour migration through the treated surface near zone and subsequent capillary condensation in the untreated material. No liquid water is in fact taken up in this case. This means that dissolved ions will not be transported into the porous structure of the material.

The silicon resin profiles which were obtained in the surface near zone with different application procedures has been measured by means of FT-IR spectroscopy. Results are described elsewhere [12].

The experimentally determined amount of water that has been taken up by the four different types of concrete after water repellent treatments is shown in Fig 2. In this case the surface has been treated with liquid silane for one hour, two and four hours followed by a second treatment of one additional hour one week later. Identical specimens have been treated with three times 200 g/m^2, with 400 plus 200 g/m^2 and with 600 g/m^2 at once of silane cream and silane gel. Between individual surface treatments one week was allowed for reaction of the water repellent agents. This type of surface treatment is now called deep impregnation. The characteristic shape of the

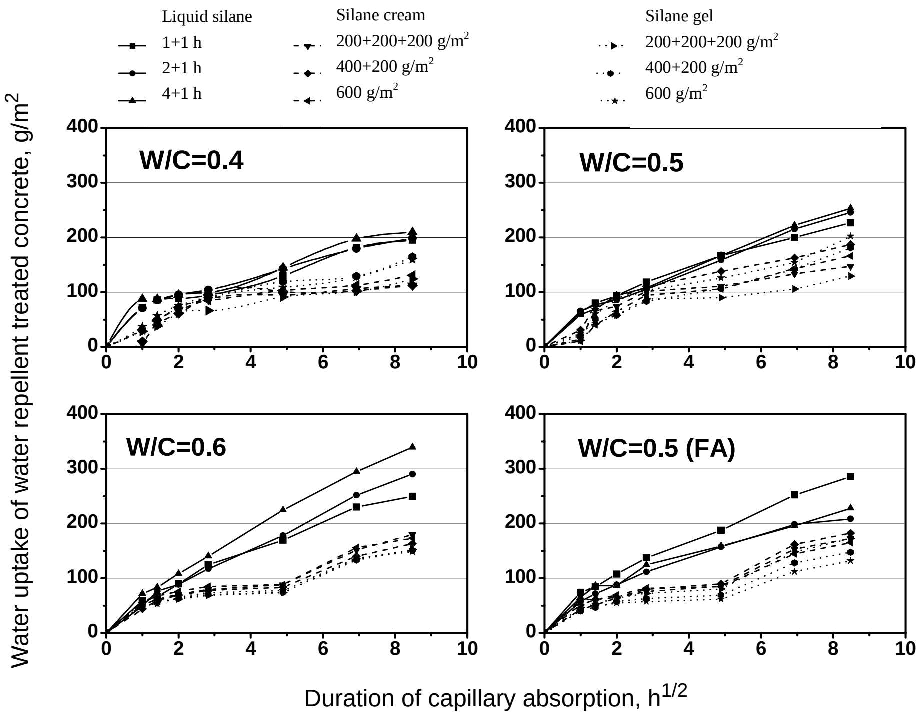

Figure 2: Uptake of water by the four different types of concrete after water repellent treatment

curves shown in Fig. 2 can be explained by the different migration processes involved in water absorption of water repellent concrete.

3.3 Chloride profiles built up in untreated concrete

As the liquid water absorption is strongly reduced by water repellent treatment it can be expected that penetration of dissolved ions such as chloride shall be reduced too. In a first test series the surface of concrete samples has been put in contact with a 3 % solution of sodium chloride for 28 days. After this exposure time chloride profiles have been measured by means of ion chromatography. Results are shown in Fig. 3.

From this figure we see that the chloride profile has a marked maximum at a characteristic penetration depth and then decreases exponentially. The observed distribution function is partly due to the fact that after the contact between the surface of concrete and the sodium chloride solution is inter-

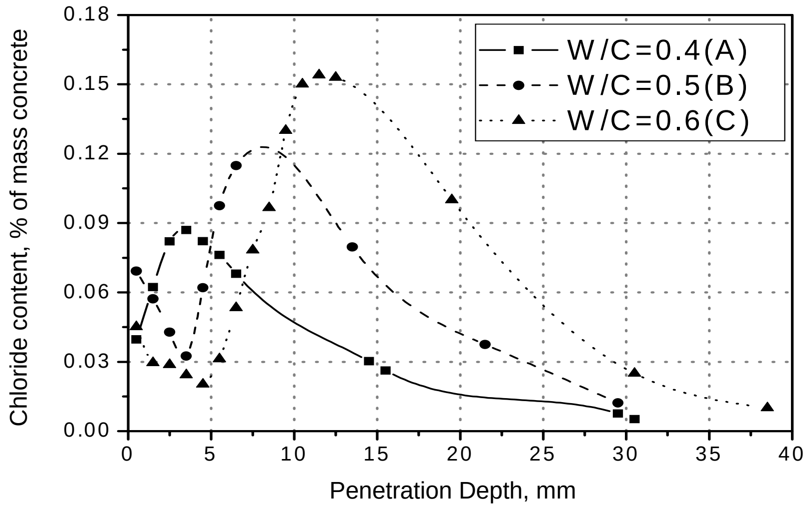

Figure 3: Chloride profiles in three different types of concrete as observed after direct contact of the surface with 3 % sodium chloride solution for 28 days

rupted chloride migrates to the surface where it is deposited as efflorescence. The shape of the distribution function changes if drying is prevented.

As it has been expected both the penetration depth and the up-taken amount of chloride increase with increasing coefficient of capillary suction. Measurement of capillary suction, for instance by means of the two chamber suction apparatus [13], may help us to predict chloride penetration into a given type of concrete.

3.4 Chloride profiles built up in water repellent concrete

In the next test series chloride penetration into water repellent concrete has been determined. In this case three different types of concrete have been impregnated first for one hour with liquid silane. The surface of concrete was in contact with liquid silane for one hour. One week later the same treatment has been repeated (1 + 1 h). Identical concrete samples have been coated with 600 g/m^2 of silane cream and a third group with 600 g/m^2. After polymerisation the treated surface of the concrete samples has been put in contact with a 3 % sodium chloride solution for 28 days. After this exposure to chloride solution the chloride distribution in the surface near zone of con-

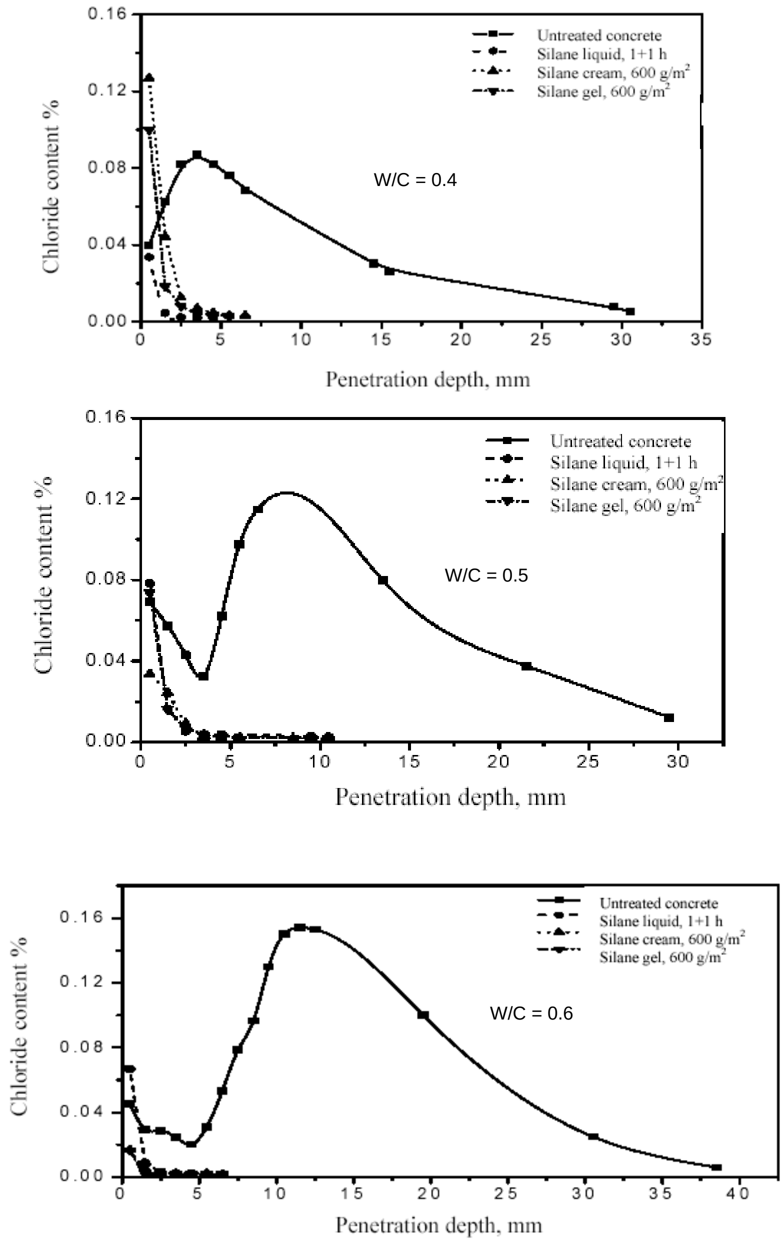

Figure 4: Chloride penetration profiles of concrete with W/C = 0.4, 0.5, and 0.6 after water repellent treatment with liquid silane, silane cream and silane gel. The chloride distribution as observed in untreated concrete samples is shown again for comparison

crete has been determined again. Results are compiled in Fig. 4. For comparison the chloride distribution of the untreated concrete as shown in Fig. 3 is shown in Fig. 4 once more. Chloride has penetrated into water repellent concrete not deeper than 2.5 mm. This small penetration depth is practically independent of the quality of concrete. The small amounts of chloride that have been detected in the surface near zone are partly fixed at the surface and partly entered coarse pores. We may conclude that deep water repellent treatment provides concrete with an efficient chloride barrier.

3.5 Chloride profiles built up in slightly treated concrete

For economic reasons it is important to know the minimum amount of water repellent agent necessary to be applied in order to establish an efficient, a reliable, and a durable chloride barrier. For this reason in another test series the amount of water repellent agent applied has been reduced substantially. The contact time between the concrete surface and liquid silane has been shortened to be 5 minutes instead of twice one hour. The applied amount of silane cream and silane gel has been reduced to 100 g/m^2 instead of 600 g/m^2. After polymerisation the impregnated samples were exposed to a 3 % sodium chloride solution for 28 days. The chloride penetration profile has been determined after this exposure period. Results are shown in Fig. 5.

Quite obviously penetration of chlorides is slowed down considerably even by this comparatively small amount of water repellent agent. But even at a depth of 5 mm penetrated chloride can still be observed. The penetration depth of the water repellent agent certainly plays a decisive role. If the thickness of the impregnated zone is less than 5 mm chloride can probably migrate along the treated surface and penetrate deeper into the concrete by diffusion [12]. Especially if we consider large surfaces with a statistical distribution of the penetration depth of chloride the latter surface treatment will not provide us with a reliable and durable chloride barrier. With a small amount of water repellent agent we can obtain a considerable reduction of chloride ingress in an aggressive environment. This may be called a chloride brake but it is not an effective chloride barrier. In some cases this may also be an interesting alternative to a chloride barrier.

More research is needed to establish a solid experimental basis for a probabilistic analysis. As a first attempt we suggest that a minimum duration of contact with liquid silane of one hour shall be allowed and a minimum of 400 g/m^2 of silane cream or silane gel shall be applied if a reliable chloride barrier is to be established. But finally the penetration depth shall be the decisive requirement that is to be respected [3].

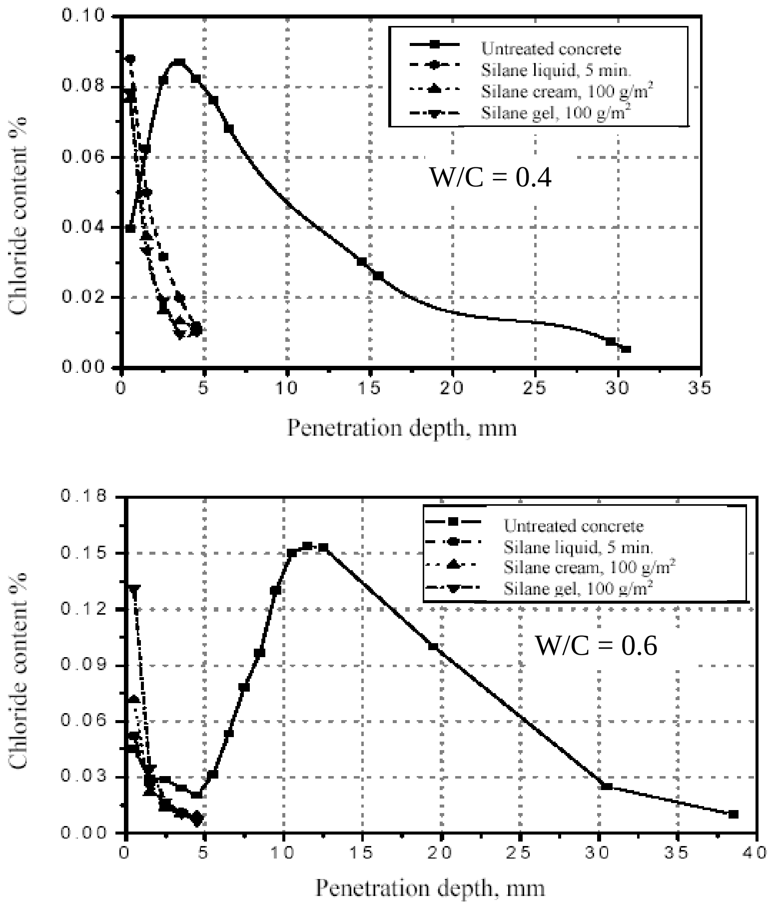

Figure 5: Chloride penetration profiles as observed in concrete treated with a minimum amount of water repellent agent

4 Conclusions

It has been shown that water repellent treatment reduces capillary suction of concrete considerably. The small amount of water that is still taken up by water repellent concrete enters as water vapour. As a consequence this transport mechanism cannot contribute to transport dissolved ions into the porous structure. If the penetration depth of the water repellent agent is not big enough small amounts of salt can probably migrate along the pore walls and then diffuse deeper into the material. For an efficient, reliable and durable chloride barrier both the penetration depth of the agent and the amount of agent in the porous system are decisive. Further research is needed to provide a solid basis of experimental data for a comprehensive reliability assessment of water repellent treatment of concrete structures.

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6 References

[1] F. H. Wittmann, *Protective coatings with water repellent agents*, in Water Repellent Treatment of Building Materials, Proceedings of Hydrophobe II, F. H. Wittmann, editor, pp. 107-118 (1998)

[2] L. Schueremans and D. Van Gemert, *Evaluation of the water repellent treatment, applied as chloride barrier on a quay wall at Zeebrugge harbour,* in Water Repellent Treatment of Building Materials, Proceedings of Hydrophobe II, F. H. Wittmann, editor, pp. 91-106 (1998)

[3] *Hydrophobieren von Betonoberflächen*, Empfehlungen für die Applikation (vorläufige Fassung), Int. J. Restoration **10**, 391-416 (2004)

[4] H. Zhan, F. H. Wittmann, and T. Zhao, *Chloride barrier for concrete in saline environment established by water repellent treatment*, Int. J. Restoration **9**, 535-550 (2003)

[5] RILEM Test Method CPC 11.2, *Absorption of water by concrete by capillarity*, TC 14-CPV (1982)

[6] H. Zhan, F. H. Wittmann, and T. Zhao, *Penetration depth of different water repellent agents*, Proc. Int. Conf. Materials Science and Restoration, MSR-IV, F. H. Wittmann, A. Gerdes, and R. Nüesch, editors, Aedificatio Publishers Freiburg, pp. 183-194 (2003)

[7] A. Gerdes and F. H. Wittmann, *Qualitätskontrolle einer hydrophobierenden Maßnahme mittels FT-IR Spektroskopie*, Int. J. Restoration **5**, 201-210 (1999)

[8] A. Gerdes, *Transport und chemische Reaktion siliciumorganischer Verbindungen in der Betonrandzone*, Building Materials Reports No. 15, Aedificatio Publishers Freiburg (2002)

[9] T. Zhao, H. Zhan, and F. H. Wittmann, *Surface treatment of concrete in order to prevent chloride penetration*, Proc. Eighth Int. Symposium on Structural Engineering for Young Experts, Xi'an, pp. 1030-1037 (2004)

[10] S. J. Meier, G. Martinola, and F. H. Wittmann, *An approach for monitoring impregnated reinforced concrete structures subject to severe chloride exposure*, Proc. Third Int. Conf. on Surface Technology with Water repellent Agents, Hydrophobe III, K. Littmann and A. E. Charola, editors, Aedificatio Publishers Freiburg, pp. 143-154 (2001)

[11] S. J. Meier, *Grundlagen und Möglichkeiten einer Hydrophobierung von Betonbauteilen*, Building Materials Reports No. 21, Aedificatio Publishers, Freiburg and Zürich (2002)

[12] H. Zhan, F. H. Wittmann and T. Zhao, *Relation between the silicon resin profiles in water repellent treated concrete and the effectiveness as a chloride barrier*, Int. J. Restoration **11** (2005), pp. 35-46

[13] S. J. Meier and F. H. Wittmann, *Entwicklung einer Zweikammer-Messzelle zur Bestimmung der kapillaren Flüssigkeitsaufnahme*, Int. J. Restoration **5**, 177-186 (1999)