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Decisive Factors for the Penetration of Silicon-Organic Compounds into Surface near Zones of Concrete

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Abstract

Water repellent treatment of concrete can lead to an effective protection of reinforced concrete structures. A. chloride barrier is just one example. This aim can be achieved only if a critical penetration depth is reached and if the necessary amount of water repellent agent has penetrated. In this contribution the penetration process is studied. It turns out that capillary suction is modified with suction time as the penetrating silane reacts chemically. The influence of reactivity of a given silane on the penetration rate has been measured. In addition it is found that silane emulsions can not penetrate the porous system of cement-based materials because they decompose. Based on the presented results criteria for a successful application technology can be formulated.

1 Introduction

In practice concrete structures are often exposed to various environmental impacts which strongly determine the service life. The treatment of concrete structures with silicon organic compounds, so-called silanes is a powerful method to prevent the uptake of aqueous salt solutions by capillary suction. For the long-term performance of an impregnation the penetration depth and the content of an active substance in the covercrete which can be characterised by penetration profiles are of utmost importance [1-3]. The shape of penetration profiles depends on several factors such as:

- duration of contact between silane and the concrete surface
- chemical reactivity of used silanes
- type of solvents that may be applied

In the following chapters the influences of these parameters on the transport of water repellent agents will be discussed.

2 Experiments

2.1 Preparation of concrete specimens

For the experimental investigations test specimens have been prepared according to SIA 162 [4]. The composition of the investigated concrete is as follows. The maximum aggregate size is 16 mm. The content of Portland Cement CEM I 42.5 is for all mixes 350 kg/m^3. The w/c ratio is 0.35, 0.40, 0.45 and 0.50, respectively. After demoulding the concrete specimens are stored at 20 C and 70% R.H. for 28 days. From these concrete elements specimens with the dimensions 70 x 70 x 75 mm^3 are cut.

2.2 Capillary suction experiments

For the characterisation of the transport of water repellent agents into concrete capillary suction experiments with different silanes have been carried out. The choosen products and selected material properties are listed in table 1.

Table 1: Relevant properties of tested water repellent agents

Product	Surface tension [mN/m]	Dynamic viscosity [mP*s]
Propyltriethoxysilane	22.7	0.95
iso-Butylriethoxysilane	23	-
n-Octyltriethoxysilane	25.5	2.08
n-Octyltriethoxysilane/water emulsion	27.9	15

For the experiments the specimens have been treated in the following way. First, the side-faces of the specimens are coated with epoxy resin. For conditioning the coated specimens are stored at 50 C and 45% R.H in a climate chamber until the constant weight is reached. After the immersion of the specimens in different commercial water repellent agents liquid uptake is measured for 24 hours. With these values the consumption of water repellent agent in g/m^2 has been calculated and plotted as a function of the square root of the duration of contact.

2.3 Analytical methods

2.3.1 Suction profiles

In order to determine the suction profiles the step-cutting method is applied. The specimens coated on the side-faces with epoxy resin are immersed in water for 24 hours. The water uptake through the impregnated covercrete over this period has been determined by weighting. Then the first 1 mm thick layer is cut off by using a specially designed milling tool. After re-conditioning at 50 C and 45% R.H. for 3 days the specimens are immersed in water again. The procedure as described above is repeated until the water uptake is comparable to the uptake of the untreated concrete. With these values the water uptake in kg/m^2 has been calculated and plotted against the square root of the duration of contact.

2.3.2 Determination of penetration profiles by means of FT-IR-spectroscopy

For the determination of the penetration profiles FT-IR-spectroscopy has been used. Fundamentals of FT-IR-spectroscopy are described in [5]. For analyses the specimens have been treated in the following way. Starting from the surface which was in contact with the water repellent agent thin layers with a thickness of 2 mm have been cut using the specially designed milling tool. The collected very fine concrete powder was dried at 105 C until the weight is constant. For the FT-IR-spectroscopy samples are prepared by using the KBr-technique. With the KBr-discs FT-IR-spectra with 10 scans in the range of 2900 to 3000 cm^{-1} are taken. The FT-IR-spectra are evaluated by the baseline method which is implemented in the software of the FT-IR spectrometer. Details of this method are described in [6-8].

Analysing standard samples with various contents of active substance specific calibration curves can be constructed for each investigated silane. With these calibration curves the content of active substance in mass-% related to the mass of concrete can be calculated.

2.3.3 Determination of liquid penetration profiles by means of neutron radiography

For the characterisation of the transport of water repellent agents into concrete neutron radiography has been applied. Neutron radiography is a method for the non-destructive examination of transport of hydrogen-containing liquids such as silanes into porous media [9-11].

For the experiment the side-faces of the specimens are sealed with aluminium foil. These specimens are put into a small dish with about 2-3 mm fluid bed of the investigated water repellent agent. This experimental set-up is placed into the neutron radiography device in front of the detector screen and is scanned across the neutron beam. Depending on the amount of hydrogen-containing compounds the intensity of the neutron beam detectable by a scintillator is reduced after crossing the specimen. For the evaluation the intensity of the detector signal is plotted against the distance from the surface placed into the liquid.

3 Results and discussion

3.1 Duration of contact

In industry concrete is often used in structures for environmental protection such as reservoirs, shelters or pipes. The applications have led to research activities on the transport of organic compounds into concrete [12-14]. Sosoro studied intensively the transport of non-reactive organic liquids such as iso-propanol in order to predict the penetration depth as a function of the duration of contact. He found out that the absorption of these organic chemicals can be sufficiently described with sufficient accurancy by the square-root-of-time relation (see equation 1) [15].

$$x = \sqrt{\frac{\sigma_l \cdot r_{eff}}{2\eta_l}} \cdot \sqrt{t} \tag{1}$$

or in a simplified form:

$$x = A_l \cdot \sqrt{t} \tag{2}$$

with

x = penetration depth [m]
r_{eff} = effective pore radius [m]
σ_l = surface tension of the liquid [mN/m]
η_l = dynamic viscosity of the liquid [mPas]
A_l = liquid absorption coefficient [kg/m^{2}s]
t = duration of contact [s]

Based on these results the validity of the square-root-of-time relation for the transport of silanes into concrete has been investigated. Figure 1 shows the test results

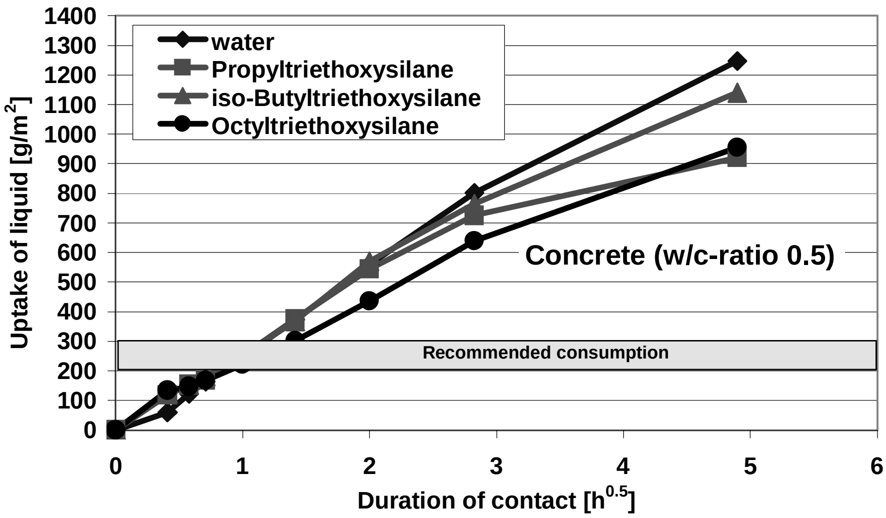

Figure 1: Capillary uptake of different liquids

obtained with different silanes. For comparision the results for water are plotted in figure 1 too. It can be seen that water absorption follows relatively well the square-root-of-time relation within 24 hours. In contrast the absorption of silane after about 6 to 8 h contact time with concrete deviates from the ideal absorption curve. The degree of deviation depends on the type of silane. This behaviour can be explained by the following processes.

It is well known that under normal climatic conditions [40% to 100% R.H.] water is adsorbed on the inner surface of capillary pores forming a film with a thickness of approximately 0.4 to 1 nm [16-18].

Therefore, instead of a liquid/solid interphase [silane/hardened cement paste] a liquid/liquid interface [silane/water] is formed in the pore systems (see figure 2 a and 2 b). According to equation (3) first formulated by Girifalco and Good the interfacial tension σ_{SW} of the silane/water interphase can be calculated [19].

(3)

The function Φ in equation (3) can be calculated with mole volumina V_S and mole volumina V_W, respectively according to equation (4).

$$\Phi = \frac{\sqrt[3]{4 \cdot V_S \cdot V_W}}{(\sqrt[3]{V_S} + \sqrt[3]{V_W})^2} \quad (4)$$

By means of values taken from the literature the value of function Φ has been estimated and the interfacial tension σ_{SW} calculated. The results of these calculations

Table 2: Calculated values for interfacial tension according to Girifalco and Good [19]

Liquid	Surface tension σ [mN/m]	Calculated interfacial tension σ_{sw} [mN/m]	
		Φ = 0.5	Φ = 0.75
Water	72.75	-	-
Propyltriethoxysilane	22.7	54.81	34.94
iso-Butyltriethoxysilane	23.0	54.85	34.40
n-Octyltriethoxysilane	25.5	55.18	33.64

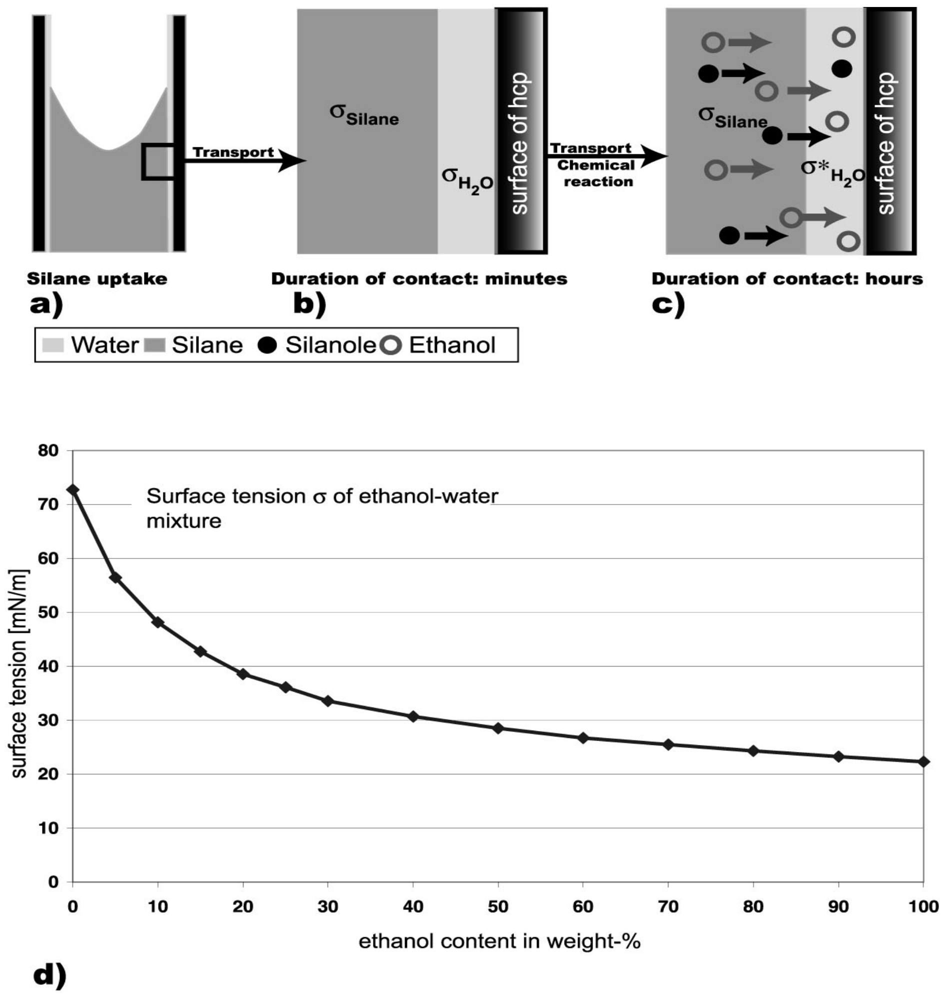

Figure 2: Silane transport in the capillaries

are presented in table 2. In fact in equation (1) the surface tension σ_{SL} must be substituted by the interfacial tension σ_{SW} . It will be shown that the interfacial tension σ_{SW} is not constant rather for decreases during the capillary uptake of silane. This effect can be explained by chemical reactions of the silanes.

After their application on the concrete surface the silane penetrates into the concrete by capillary suction forming the interphase as described above. After a fewhours the silane hydrolyses under the formation of water-soluble silanols and ethanol which migrate into the water film (Figure 2 c). It is well known that even a small amount of alcohol (> 5 weight-%) leads to a siginifcant decrease of the interfacial tension (Figure 2 d). Therefore, as a result of the decrease of the liquid absorption coefficient A_l (equation 2) the silane absorption deviates from the ideal absorption curve depending on the chemical reactivity of the silanes. But it should be noted that silane absorption can be predicted by means of the square-root-of time relation if the duration of contact is below 8 hours and if the silane absorption coefficient A_S is known.

3.2 Chemical reactivity of silanes

It has been shown in chapter 3.1 that the deviation from the ideal absorption curve depends on the chemical reactivity of the silane. The chemical reactions which take place in the pores of the concrete can be subdivided into two key reactions: hydrolysis of the trialkoxysilanes to silanetriols and condensation of the silanetriols to siloxanes. The rate-determining step of the silane polymerisation is the hydrolysis reaction. The rate of hydrolysis depends on several factors such as:

- **pH-value**
  Hydrolysis can be catalyzed by bases. The slowest rate is aproximately at pH 7. Each change of pH by 1 unit of pH towords more basic direction produces a ten-fold acceleration in rate of hydrolysis [20].
- **structure of the alkoxy groups**
  Large alkoxy groups hydrolyze more slowly than small ones. The rate of hydrolysis for methoxy groups is roughly speaking 5 times higher as compared to ethoxy groups [20].
- **the structure of the alkyl group**
  In particular, for the investigated silanes the structure of the alkyl group plays an important role for the reactivity. Studies by Brand et. al and Osterholtz have shown that with increasing number of C-atoms the hydrolysis tends to decrease [20, 21]. Also steric hindrance by silicon in branched molecules such as the iso-butyl group leads to a decrease of reactivity.

Summarizing it can be said that the rate of hydrolysis increases in the following sequence: iso-butyl >> n-octyl >> propyl. In the same order the time when the absorption curve deviates from the the ideal function decreases for the silanes under invvestigation.

3.3 Type of solvents

In recent years aqueous silane emulsions with low viscosity have been suggested and applied for the impregnation of concrete mainly for ecological reasons. Emulsions are dispersed systems consisting of two insoluble liquids. For the formation of emulsions silane, water and emulsifier are mixed. The mechanical energy of mixing disperses the silane phase into the aqueous phase under the formation of silane droplets with a diameter of 1 to 100 microns. The emulsifier serve to facilitate the droplet formation and to stabilize the emulsion after formation [22].

However, practical experiences and results from experiments carried out in the laboratory have shown that the penetration depth does not exceed 0.5-1 mm even for a duration of contact of 24 h (figure 3).

In order to understand the mechanisms which prevent the transport of silane into concrete capillary suction experiments have been carried out. In contrast to the results shown in fig. 3 the liquid penetration profiles determined by means of neutron radiography show that the penetration depth of the liquid front is in the range of 3 mm for a duration of contact of 4 h, and in the range of 7 mm for a duration of contact of 24 h (figure 4).

These experimental data indicate that during the suction process demulsification on the concrete surface takes place. As a result of the phase separation water

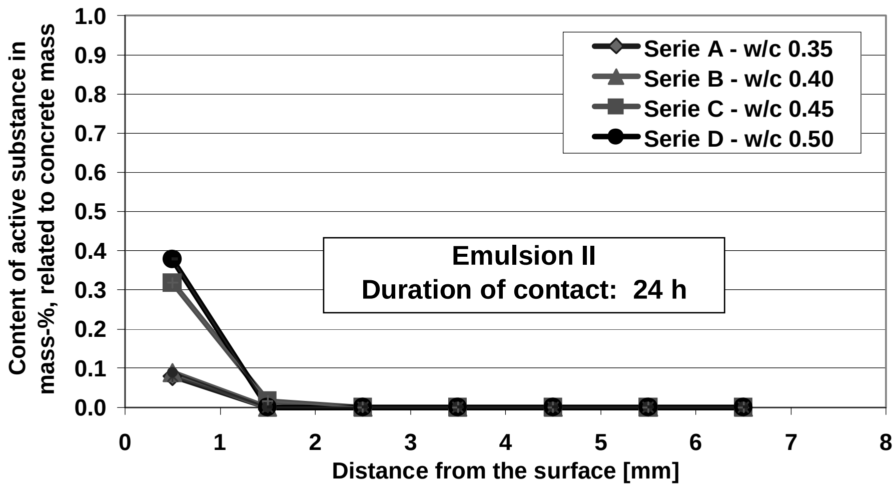

Figure 3: Penetration profiles for concrete treated with emulsions

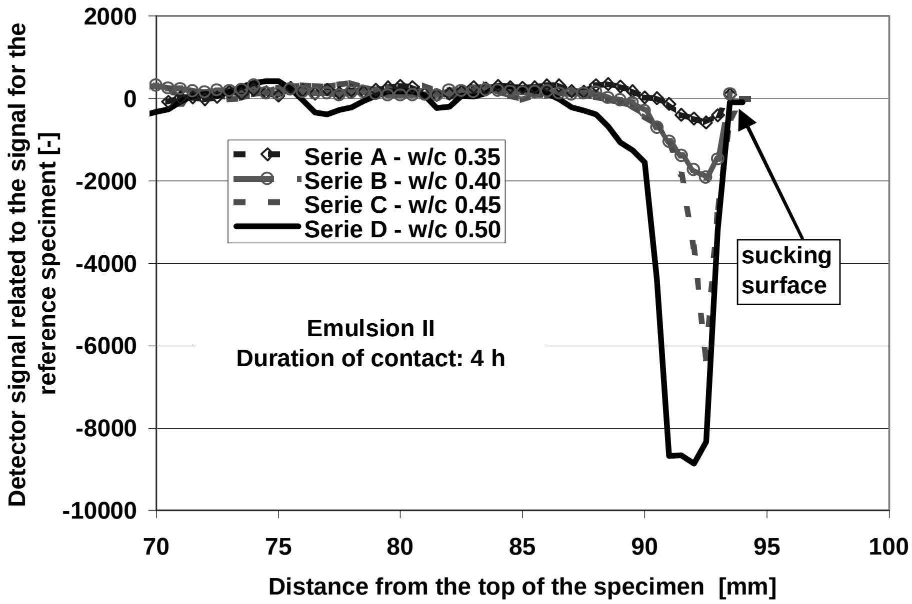

Figure 4: Liquid penetration profiles for concrete treated with emulsions as observed by neutron radiography

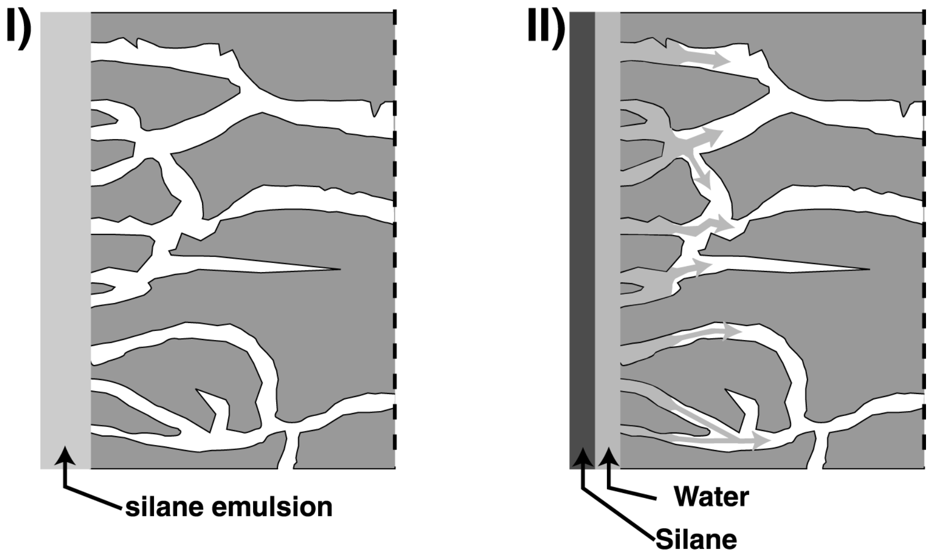

Figure 5: Capillary uptake of an aqueous silane emulsion

penetrates into the covercrete only, while the silane evaporates on the concrete surface (figure 5).

Mechanisms which lead to the breaking of an emulsion are very complex, however, the following effects can lead to phase separation [23]:

- **Filter effect**
  Porous media such as concrete with pores in the range of 0.1 to 10 microns can act as a filter which separates droplets and aqueous phase.
- **Effect of electrolyte**
  Cations dissolved in the pore solution can destabilize the emulsion by reducing the repulsive forces between the dispersed droplets.
- **Effect of organic compounds**
  Organic compounds such as alcohols act as demulsifiers.
- **Adsorption of emulsifier**
  Emulsifier may be adsorbed on the surface of the capillary pores. The remaining emulsifier concentration in the solution is not sufficient for the stabilisation of the emulsion

Based on these results it can not be recommended to apply emulsion systems for the water repellent treatment of cement-based materials.

4 Conclusions

From the results presented in this contribution the following conclusions can be drawn:

- The silane absorption can be predicted by the square-root-of-time relation if the duration of contact is below 8 hours and if the silane absorption coefficient A_S is known.
- Physical properties which determine the transport process such as interfacial tension σ and dynamic viscosity η vary over the contact time as a result of chemical reactions which take place during the transport into the pore system. This means that the capillary transport of silane into the pore system is influenced by chemical reactions.
- The deviation from the ideal adsorption curve depends on the chemical reactivity of the silanes which is strongly dependent on the pH value, the structure of the alkoxy groups and alkyl groups.
- Due to chemical-physical effects emulsions may break down on the concrete surface during the suction process. As a result of phase separation water penetrates into the covercrete while silane evaporates from the concrete surface. Therefore, emulsions are not suitable for the treatment of concrete structures.

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