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Chemical Reactivity of Silanes in Cement-Based Materials

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Abstract

The protection of concrete structures by means of water repellent agents has become a well-accepted method in practice. One of the reason for that is the better understanding of factors such as chemical reactivity and physical properties of the silanes which determine the performance and durability of water repellent treatments. However, there is a lack of knowledge about the parameters influencing the reactive transport of silanes in concrete. In this contribution a new device for an in-situ measurement of the kinetic of hydrolysis is presented. The experiment is suitable to characterise the influence of the chemical structure on the chemical reactivity. This relationship is important for the development of new silane-based products with a high performance and durability. Further, it will be shown that not only the chemical reactivity of the silanes but also the solid phase (CSH-gel) plays an important role for the reactive transport.

1 Introduction

In practice the application of silane-based water repellent agents becomes more and more a well-accepted technique for the preventive protection of concrete structures. One of the reasons for that are the research activities in the recent years which have lead to a better understanding of factors determining the performance and durability of water repellent treatments [1-4].

Two of the most important factors are the penetration depth and the content of silicon resin in the covercrete which can be characterised by penetration profiles [5-6].

The investigation of the interactions between silanes and cement-based materials has shown that the shape of the penetration profiles depends on several factors such as:

- pore structure of the treated concrete
- physical properties of silane, e.g. surface tension
- chemical reactivity of concrete and silane, respectively [7].

Therefore, the uptake of the silanes can be considered as a reactive transport of an organic liquid in a porous media. Starting from this point a model has been developed which describes the reactive transport of silane qualitatively.

2 Reactive transport of silane into concrete

2.1 Capillary transport of liquids

The capillary transport of water in concrete are often described by the square-root-of-time relation (see equation 1) [8]. According to this equation the penetration depth depends on different parameters such as the surface tension σ, which is mostly the driving force for the transport, the viscosity η of the liquid, the effective radius r_{eff} of the porous material and the contact time t.

Sosoro has shown, that the transport of non-reactive organic liquids can also be described with sufficient accurancy by this equation [9].

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

or in a simplified form:

$$x = A_l \cdot \sqrt{t} \qquad (2)$$

with

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

In opposite to that capillary suction experiments with silanes show that the measured absorption curves deviate from the ideal absorption curve after about 6 to 8 h contact time with concrete. The uptaked amount for all investigated silanes is lower compared to the theoretical amount which can be estimated with the ideal absorption curve. Summarizing it can be said that the degree of deviation increases in the following sequence: iso-butyl >> n-octyl >> propyl [10]. Due to the fact that the values of the surface tension for all silanes are very similar it can be expected that the chemical reactivity of the silanes plays an important role for the transport.

2.2 Chemical reactivity of silanes

The manufacturing of silane-based products is a technical process with a high economical importance. Therefore, a lot of investigations have been carried out to characterise the factors which influence the mechanism and kinetic of the polymerisation.

In principle, the polymerisation process can be subdivided into two key reactions:

- hydrolysis of the trialkoxysilanes to silantriols and ethanol
- polycondensation of the silantriols to siloxanes

According to the studies of Arkles et. al and Osterholz the rate-determining step of the silane polymerisation is the hydrolysis. The rate of hydrolysis depends on several factors such as [11,12]:

- **pH-value**
  Hydrolysis can be catalyzed by acids and bases. The slowest rate is approximately at pH 7.

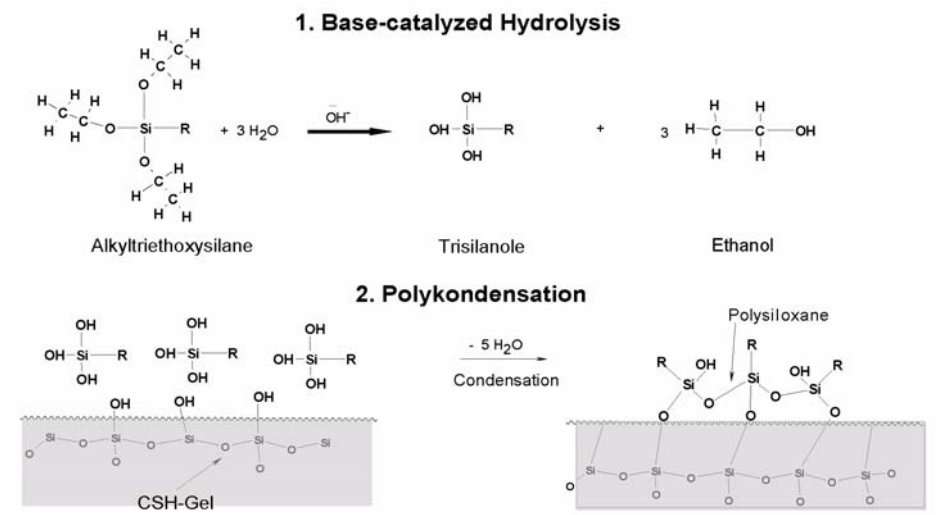

Figure 1: Chemical reactions of silanes

- **structure of the alkoxy groups**
  Large alkoxy groups hydrolyze more slowly than small ones. The hydrolysis rate for methoxy groups is roughly speaking 5 times higher compared to ethoxy groups.
- **the structure of the alkyl group**
  The structure of the alkyl group plays an important role for the reactivity. Within increasing number of C-atoms the hydrolysis rate tends to decrease.

For concrete it can be expected that during the transport hydrolysis of silane takes place liberating ethanol and silantriols. In the next step the silantriols condensate to siloxanes which are bounded to OH-groups on the CSH- surfaces (Fig. 1).

2.3 Reactive transport of silane in concrete

With experimental data and data from literature the following model for the reactive transport of silanes in concrete has been developed.

During the first minutes after contact an interface between silane and the water film which covers the pore surface under normal climatic conditions (40% to 100% R.H.) is formed (Fig. 2, a and b) [13-15].

Therefore, in equation (1) the surface tension σ_{SL} must be substituted by the interfacial tension σ_{SW} . According to Girifalco and Good the interfacial tension σ_{SW} of the silane/water interface can be calculated with the values for

Table 1: Calculated values for interfacial tension according to Girifalco and Good [16]

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

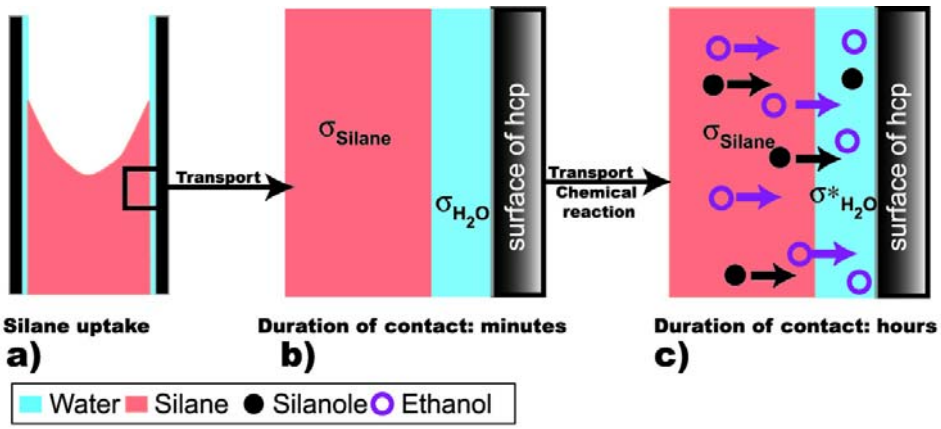

Figure 2: Transport of silanes in cement-based materials

the surface tension of silane and water, respectively [16]. Typical results for different silanes are listed in table 1.

During the next hours the hydrolysis of the silane under the formation of ethanol and silantriols takes place. Both species are water-soluble and migrate into the water film (Fig. 2,c). It is well known that the surface tension of water-ethanol-mixtures is significantly lower compared to the surface tension of pure water. In consequence of the reduced surface tension of the water/ethanol film the interfacial tension σ_{SW} is also reduced and therefore,

the driving force for the capillary transport decrease. With this qualitative model the influence of the silane reactivity on the transport process and consequentially the penetration depth in concrete can be explained.

But, for a realistic model describing the reactive transport the kinetics of the hydrolysis (e.g. order of reaction, rate constant) for the different silanes must be known more detailed. For that an experimental method has been developed which allows the in-situ measurement of the kinetic of silane hydrolysis in concrete.

3 Experiments

3.1 Preparation of concrete powder

For the experiments concrete has been prepared according to EN 206 [17]. The composition of the used concrete is as follows. The maximum aggregate size is 16 mm. The content of Portland Cement CEM I 42.5 is 350 kg/m^3. The w/c ratio is 0.45. After demoulding the concrete elements 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. After that the specimens have been crushed and grinded. The concrete powder is stored in a CO_2-free atmosphere until the material is used for the reactor experiment.

3.2 Reactor Experiment - set-up

The set-up of the new experiment based on a device for High-Performance Liquid Chromatography (HPLC) is shown in fig. 1. For the preparation of the experiment the column (made of stainless steel with a diameter of 8 mm and a length of 50 cm) must be packed with concrete powder. For that the concrete powder is dispersed in deionised water. The column is then filled with this dispersion. After preparation the columm is screwed and connected to the injection valve.

At the beginning of the experiment a solution of saturated calcium hydroxide is pumped through the column with a flow of 0.05 ml/min. For starting the experiment 1 ml of the silane which should be investigated is injected by the injection valve. Meanwhile the experiment is running the output is collected at the end of the column for a time intervall of 5 minutes. After collecting each of these fractions are analysed by Headspace-GC-MS immediately.

After completion of the experiment the column is drilled out step by step using a drilling machine. For each step (1 cm) the samples has been collected and stored in small glasses. In these samples the content of active substance has been detemined by means of FT-IR-spectroscopy.

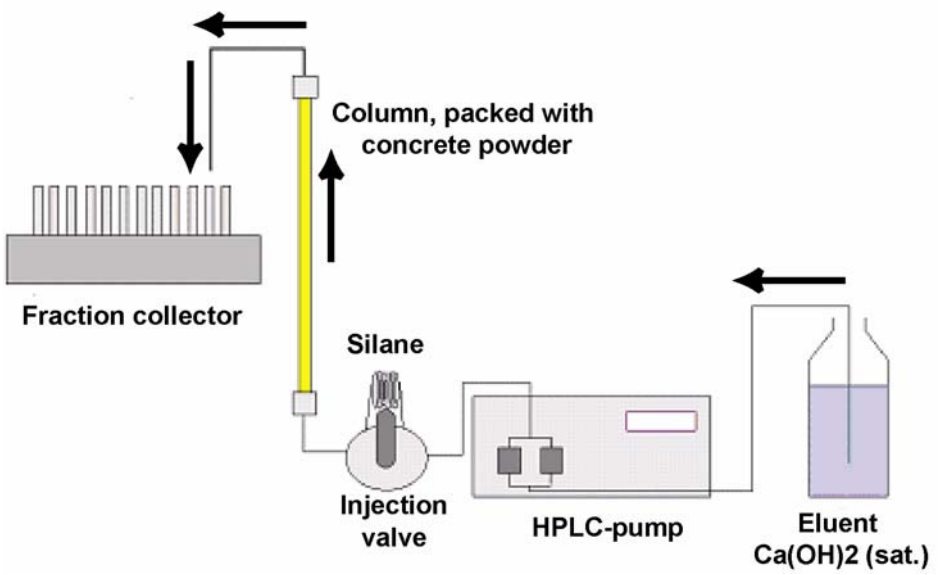

Figure 3: Reactor Experiment - Set-up

3.3 Determination of the polysiloxane distribution by means of FT-IR-spectroscopy

For the determination of the polysiloxane distribution in the column FT-IR-spectroscopy has been used. Fundamentals of FT-IR-spectroscopy are described in [18]. For the analyses the samples have been treated in the following way. 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 [5,10].

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.

4 Results and discussion

In order to characterise the kinetic of the hydrolysis process different experiments with the so-called reactor device has been carried out. In this experiment the rate of reaction can be determined by the amount of ethanol which

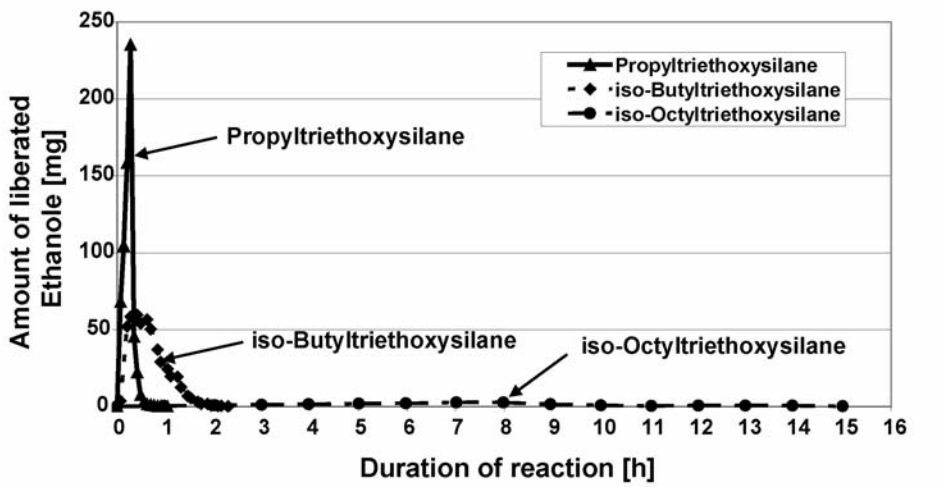

Figure 4: Rate of reaction for different silanes

is liberated during the hydrolysis. The experimental parameters are described in more detail in chapter 3.2.

First of all, it can be shown that no breakthrough of silanes occurs during the experiment. In all fractions analysed with Headspace-GC-MS only ethanol is detectable. Results of these experiments are shown in fig. 4.

For propyltriethoxysilane the peak maximum for the ethanol liberation can be observed after approximately 8 hours. In comparision to that the peak maximum for the iso-butyltriethoxysilane can be observed after 16 hours. The curve for the octyltriethoxysilane is quite different compared to the curves for the silanes discussed before. The shape of the curve is flat. The peak observed after a duration of 7.5 days is very small.

Furthermore, there is a difference in the amount of ethanol which is liberated by hydrolysis of propyltriethoxysilane or iso-butyltriethoxysilane and iso-octyltriethoxysilane, respectively.

With the amount of silane injected into the column the maximum amount of ethanol liberated by hydrolysis can be calculated. The comparision of these theoretical values with the values calculated from the results of the chemical analysis shows that nearly 100% of propyltriethoxysilane and iso-butyltri-ethoxysilane have reacted under the formation of polysiloxane. In opposite to that only 50% of the theoretical amount of ethanol is liberated by iso-ocyl-triethoxysilane after a duration of 15 days.

The results indicate that the rate of hydrolysis is strongly influenced by the chemical structure of the investigated silanes. It can be noticed that with an

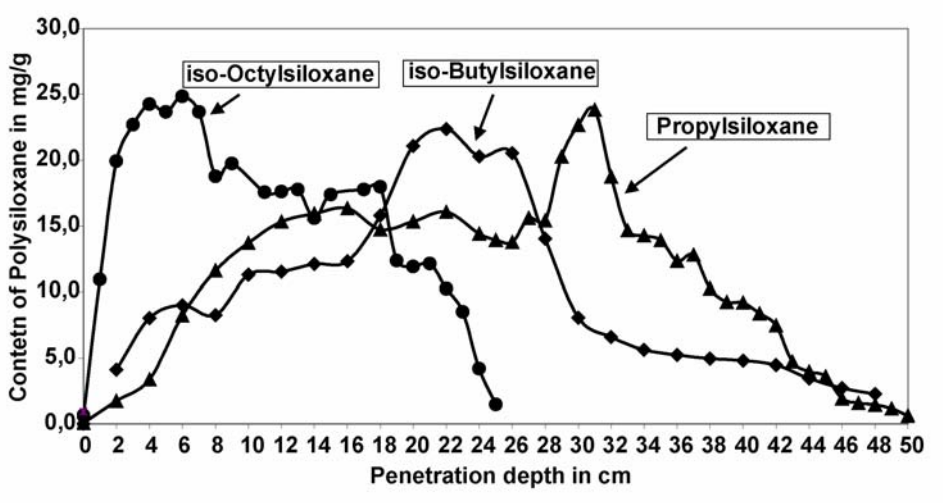

Figure 5: : Siloxane distribution in the column

increasing number of the C-atoms in the alkyl group the rate of hydrolysis decrease. This effect is obvious for iso-ocyltriethoxysilane. After liberation of 1 to 2 alkoxy groups the iso-ocyltriethoxysilanol is relative stable and further hydrolysis takes place with a very low rate.

The rate of hydrolysis should also influence the rate of condensation. Higher rates of hydrolysis lead to higher concentrations of reactive silanols in the pore solution and therefore, a shift of the chemical equilibrium to higher rates of condensation should occur.

To get information about the chemical equilibrium of hydrolysis and polycondensation the distribution of the polysiloxanes in the column has been determined by means of FT-IR-spectroscopy. The results of this investigation are presented in fig. 5.

In spite of the very low rate of hydrolysis for iso-octytriethoxysilane most of iso-octylsiloxane is fixed on the solid phase in the first half of the column. For propyltriethoxysilane the penetration profile is quite different compared to the profile determined for iso-octylsiloxane. Most of propylsiloxane formed during the very fast hydrolysis of propyltriethoxysilane is fixed in the second half of the column. Following the results for the liberation of ethanol the reverse of the obtained distribution has been expected.

This results can be interpreted in the following way. As already mentioned iso-ocyltriethoxysilane reacts under liberation of 1-2 ethanol molecules to iso-ocyltriethoxysilanol. But, it seems to be that the expected intra-molecular condensation of two iso-ocyltriethoxysilanol molecules is hindered

because of steric reasons. So, at first the silanols react very fast with the OH-groups of the CSH-gel. Further hydrolysis and the intermolecular condensation between the molecules fixed on CSH-gel is also retarded by the steric effect.

In opposite to that propyltriethoxysilane reacts very fast under liberation of all ethoxy groups. This leads to a high silanol concentration in the pore solution. The inter-molecular poycondensation of this type of silanols is not sterical hindered, thus the probability of this reaction is very high. The probability of the intra-molecular reaction between the silanols and CSH-gel do not increase until the silanol concentration in the pore solution is reduced by condensation. This will be the case at the end of the column.

The results presented here indicate that not only the rate of hydrolysis of the silanes which depends strongly on the chemical structure but also interactions between the macromolecules formed in the pore solution and the solid phase “CSH-gel” play an important role. Further investigations must be carried out to clarify the chemical reactions taking place during the “reactive transport” of silanes in concrete in detail.

5 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 chemical reactivity of the silanes depends strongly on the structure of the alkoxy groups and alkyl groups.
- For the reactive transport of silanes not only the chemical structure of the silanes but also the solid phase „CSG-gel“ plays an important role.
- With the results presented here a numerical model for the reactive transport of silanes in concrete will be developed.
- The reactor experiment can be used to establish a relationship between chemical structure and chemical reactivity which is important for the development of new silane-based products with a higher performance and long-term durability.

6 Literature

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