Hydrophobe VI
6th International Conference on Water Repellent Treatment of Building Materials
Aedificatio Publishers, 69 - 80 (2011)

Combination of Quantum-mechanical and Experimental Investigations for the Development of a Model of the Size and Distribution of Silane Oligomers on the Pore Surface of Mineral Based Material

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Abstract

Silicon organic compounds (e.g. Alkyltrialkoxysilanes) can be used to protect cement based materials from the intrusion of water and therein solved substances.

Less is known about the processes whilst the transport, because the Alkyltriethoxysilanes, ATES, follow a complex reaction mechanism, which is governed through factors like temperature, pH-value and concentration. Additionally the interactions with the mineral surface are not clarified.

The interactions between the mineral surface and the ATES are little accessible through experimental investigations, so molecular modelling methods can be used in addition. The combination of experimental data like the ethanol-release and the product distribution of the polycondensation and of semi-empirical-modelling methods allows some suggestions for the oligomer-size and distribution of the ATES. The nitrogen-sorption data of some treated mineral based materials are analysed with an NLDFT-method to calculate the sorption behaviour of materials with an SiO_2- or Carbon-surface. The difference between the experimental and theoretical data is applied to calculate a *fitting error*, which can be seen as a criterion for the similarity of the theoretic assumption to the real measured surface.

Keywords: Alkyltriethoxysilanes, mineral based material, pore-surface, molecular modelling, nitrogen-sorption

1 Basics

1.1 Alkyltriethoxysilanes

The polycondensation of ATES can be subdivided into two reaction steps, first hydrolysis, followed by condensation. Both parts of the polycondensation are influenced through a multitude of factors, like the structure of the ATES-molecule and the reaction conditions. The longer and more branched the alkylgroup of the ATES is, the slower the polycondensation proceeds. Alkaline conditions retard the reaction as well [1].

1.2 Mineral based materials

Concrete is a very complex system with a variety of chemical properties. To reduce the complexity, some of the principal constituents of concrete like hydrated CEM I, C_3S and tobermorite are investigated. The hydrated cement represents the cementstone, the hydrated C_3S the CSH-Gel and tobermorite is a kind of crystalline product correspondent of the CSH-Gel [2].

Cement based materials are porous. At the pore surface there are partly deprotonated silanol groups. The ATES are transported through capillary suction. Whilst the transport the polycondensation starts in the alkaline pore solution. The mineral pore surface influences the polycondensation, which can be seen e. g. at the ethanol-release [3]. The products of the ATES-polycondensation can be either covalently or loosely attached to the surface to build the water repellent film into the pore space.

1.3 Computational Chemistry

The Computational Chemistry bases upon the quantum mechanical concepts. It can be used to clarify experimental unaccessible processes. Like experimental results, modelling results have to be treated with regard to the validity of the used modelling method.

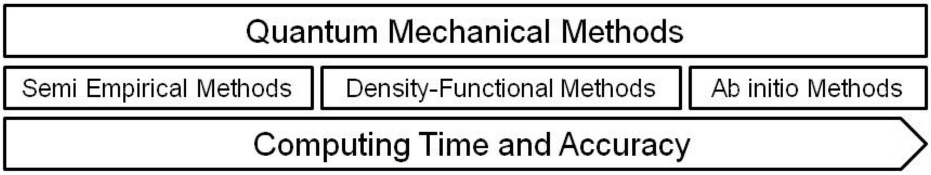

Figure 1: Overview modelling methods

Fundamental of all quantum mechanical methods is the so called *Schrödinger equation*, which is analytically unsolvable. One of the main problems of all modelling methods is the calculation of the electron-correlation, this means the dependence of the state of each single electron of all others at any point of time. Therefore for the different methods simplifications are adopted (Figure 1). The Hartree-Fock-(HF)-method is used to get the solutions for the many-body problem. The many-body wavefunction is written as a product of one-electron wavefunctions. The wavefunctions are build through a linear combination of atomic orbitals (LCAO). These orbitals are approximated through Slater- or Gauss-type-functions. The HF-formalism to solve the wavefunctions leads to a multitude of integrals. The semi-empirical methods use experimental determined parameters in the Hartree-Fock-equations and only distinguish between the inner (so-called core) and valence electrons. Semi-empirical parameters are continuously improved and adapted to experimental data. These models can handle large molecules and yield good results for suitable molecules with well parameterised atoms in the HF-formalismDensity functional methods calculate the energy of a system as function of the electron density, not as a function of the coordinates of each electron, thus reducing the complexity of the problem significantly, because fewer equations are required [4].

1.4 Nitrogen-Sorption

Through the sorption of gases (mostly nitrogen or noble gases), the BET (Brunauer-Emmet-Teller)-method can be used to determine the specific surface area (SSA) and pore size distribution of grained and porous materials. The absorbed volume of the gas is measured as a function of the pressure at constant temperature. Basic assumption of the method is, that the interaction between the sorbed molecules is small and of the same magnitude as the bonding energy at the surface. So, several layers can be sorbed and each layer can be described as a Langmuir-isotherm: the sorption-velocity is proportional to the pressure and the amount of free-sorption sites while the desorption-velocity is proportional to the number of occupied sites [5][6].

The measured isotherms are the base for all subsequent evaluation methods such as BET, Barrett-Joyner-Halenda (BJH) or Non-Local-Density-Functional-Theory (NLDFT). To obtain the pore size distribution, the measured isotherms are usually analysed with the classical BJH-method. While for the Quantachrome-software, a more advanced method is available (whith the so called NLDFT method. These methods consider characteristics of certain surfaces like SiO_2 or carbon. Therefore the gas-sorption of a material with a certain pore size distribution and defined surface properties is calculated with respect to the desorption branch and compared to the measured one. This comparison results in a so called *fitting error* which reflects the match of both. This offers a possibility to account for surface characteristics and properties, which is impossible with the conventional BJH-method [7][8][9].

Further information can be attained from the plot of the sorbed volume of one sample to another at the same relative pressure p/p_0. If the materials have similar pore size distributions and nitrogen-affinity, the plot pattern is a bisectrix. If a straight line with another slope is obtained, one sample sorbs a higher N_2-volume or has a higher N_2-affinity. In case of a non-linear plot, the pore size distribution differs. This allows a direct model independent comparison of the behaviour of different samples.

2 Materials and results

2.1 Sample preparation

Tobermorite, cement-stone and CSH-gel are treated with Propyltriethoxysilane, PTES and iso-Octyltriethoxysilane iOTES. Cement-stone and CSH-gel with a water/cement (w/c) ratio of 0,4 are cuboid-formed (10x5x5 mm), tobermorite is powdery (< 200 µm). The cuboids are treated with 2 ml of silane whereas in case of tobermorite 5g powder is stirred with 2 ml of $Ca(OH)_2$ and 2 ml of silane. After 21 days, the samples are washed with cyclohexane to remove excessive silanes and dried at 293 K and 3 mbar.

2.2 BET-examination

2.2.1 Isotherms and specific surface area

The BET-examinations are carried out with an “Autosorb 1 MP” from Quantachrome. Samples are dried at 313 K till constant weight. Temperature for measurement is 77 K with liquid N_2.

In Fig. 2 a)-c) the isotherms of the tested mineral materials are illustrated, while in d) the SSA. For the tested materials, the PTES-treated-sample shows the highest N_2-Sorption. As shown in figure 2d), the SSA is the highest for these samples compared to the untreated and the with iOTES-treated ones.

2.2.2 Comparison of the N_2-sorption behaviour

To compare the pore size distribution and the nitrogen affinity of untreated and treated samples, the sorbed N_2-volumes at the same p/p_0 are plotted (Fig. 3 a-c).

The PTES leads to a material with higher pore volume or higher N_2-affinity for the three mineral materials and this for the whole range of p/p_0. For iOTES-treated tobermorite the plot against untreated tobermorite shows a straight line with a slope smaller than the one of the bisectrix. For CSH-gel, in case of a low p/p_0 the sorbed N_2-volume is higher, while lower in case of a higher p/p_0 . In cement stone, the iOTES-sample shows for small p/p_0 the same behaviour as the untreated material, at higher p/p_0 less N_2 is sorbed caused by a lower pore volume or N_2-affinity.

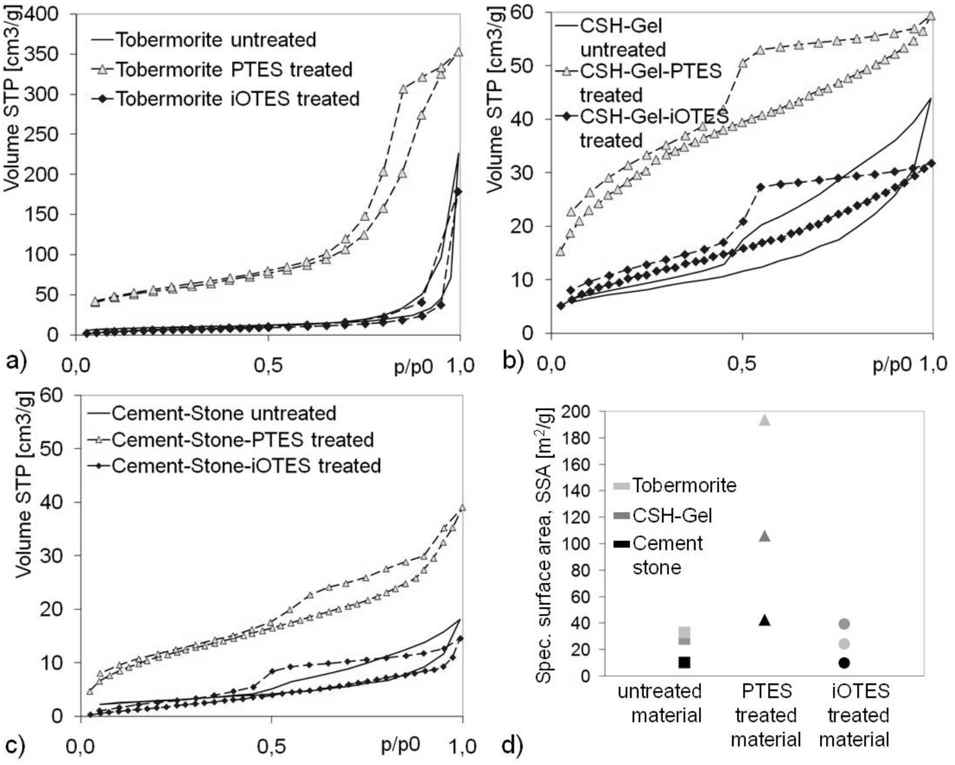

Figure 2: Isotherms for untreated and with PTES and iOTES treated samples of a) tobermorite, b) CSH-gel, c) cement stone and d) SSA of these samples

2.2.3 Fitting error

The NLDFT-modelling is done with the Quantachrome-software. The *N_2 @ 77 K on silica* (cylindric pore, NLDFT, equilibrium model)- and the *N_2 @ 77 K on carbon* (cylindric pore, NLDFT, equilibrium model)-kernel are used. With these kernels a theoretic N_2-sorption in a cylindric pore-system at 77 K on either a silica- or a carbon-surface is calculated with NLDFT-methods. The technical term for the methods is “kernel” [10].

Figure 3 shows the *fitting error* in % for the analysis with the two kernels. The *N_2 @ 77 K on silica* is designated as “*silica*”, the *N_2 @ 77 K on carbon* as “*carbon*”.

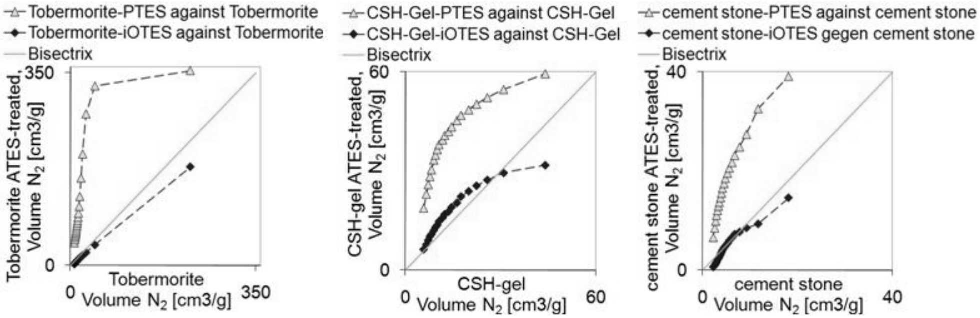

Figure 3: Plots of sorbed N_2-Volume for with PTES and iOTES treated samples of a) tobermorite, b) CSH-gel, c) cement stone with reference to the untreated material

The tobermorite shows for both treated and untreated samples better *fitting errors* in case of a analysis with the *silica*-kernel, which determines a silica surface in cylindric pores as explained before. The slightly bigger difference can be found for the untreated sample while the smallest for the PTES-sample. The ones for the *carbon*-analysis of the un- and with iOTES-treated sample are very high. For the CSH-gel, the kind of the used kernel hasn’t as much impact on the fitting error as for the other two mineral materials. For the un- and with PTES-treated cement stone, the *fitting error* for the *silica* surface-analysis is the lowest. The *fitting error* of the *carbon*-analysis for iOTES treated cement stone is high, but the one for the *silica*-analysis is higher.

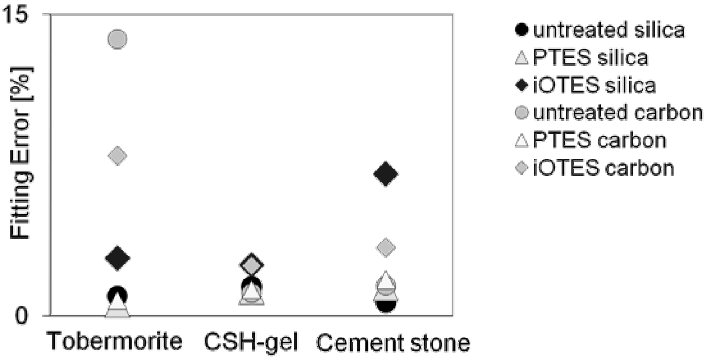

Figure 4: Fitting error of the silica-and carbon-analysis for untreated and with PTES and iOTES treated tobermorite, CSH-gel and cement stone in %

2.3 Semi empirical modelling

For the semi-empirical modelling, the “Spartan®”-software from Wavefunction Inc. [11] is used. One of the possible methods is PM3, a widespread used method. It contains almost all atoms with a broad statistical founded parametrisation. It is suitable for the modelling of molecular geometries and even for hydrogen bonds, which are problematic for some other methods.

For the assembling of the ATES-oligomer, the energy of states are modelled in a system, starting with eight monomers and 26 water molecules. In each step a Si-O-Si-bond is formed under the release of a water molecule. The state is geometry-optimised semi-empirical (PM3). For the octylsilane-systems, the propylsilane-states are copied and just the alkylgroups are enlarged to get a similar arrangement of the molecules, especially of the water molecules and the hydrogen bonds. Then the geometries of all these states are optimised. From all the states the energies in a.u. are calculated and compared. It is a largely known, fundamental thermodynamic principle, that systems try to reach a state with lower energy. So, if there is a possibility, a reaction will run into the direction of the state with lower energy.

For the propylsilane the energy-values decrease till the experimental detected main product is formed. The values of the octylsilane show a little increase for the tetramer (S4) and octamer (S8) on the way to the main product [12]. This is summarised in Table 1.

Table 1: Watermolecules and energies of the polycondensation states of the ATES-reaction to the main product

Step	Oligomer	Number of Water-molecules	Energy PTES (a.u.)	Energy iOTES (a.u.)
S1	Monomer	26	-5,9295	-6,2549
S2	Dimer	27	-5,9379	-6,2874
S3	Trimer	28	-5,9486	-6,2992
S4	Tetramer	29	-5,9577	**-6,2973**
S5	Tetramer, ring	30	-5,9650	-6,3055
S6	Pentamer	31	-5,9845	-6,3067
S7	Hexamer	32	-5,9849	-6,3165
S8	Hexamer, ring	33	-5,9863	**-6,3145**
S9	Heptamer	34	-6,0067	-6,3295
S10	Heptamer, ring	35	-6,0120	-6,3350

3 Discussion

3.1 Reaction behaviour of the ATES

From measurements of the ethanol release some differences in the reaction behaviour of PTES and iOTES are known. The experimental results show a fast ethanol release for PTES (97% after 1h) and a slow one (98% after 198h) for iOTES in pure alkaline (pH=12,6) solution. The addition of cement stone retards the ethanol release in both cases (for PTES almost 100% after 24h) and reduces it for iOTES (77% after 216h) [3].

If the silanemolecules follow the same reaction sequence whilst the condensation the energy curve shows for the iOTES an increase at the step (S4) and just a very little decrease at S6. This could be an indication for the slower progression of the condensation. Assuming that the moment of the interaction between silane and the mineral surface is only influenced through the transportation process and not the reaction sequence, the iOTES-oligomer interacting with the surface would be a smaller one than a PTES-oligomer.

3.2 Surface characteristics of un- and treated material

In this case, the fitting error is used to describe the surface characteristics. The basic assumption is, that the closer the calculated model-surface approaches the experimental values, the smaller the *fitting error* should be. The *carbon*-analysis *fitting error* should be smaller in case the mineral surface is covered with silane-oligomers of which the alkylgroups protrude into the pore space. In this way the mineral surface loses its silica-characteristics and attains carbon ones.

The tobermorite, despite the treatment, retains its silica characteristics, but for the PTES treated sample the difference between the *silica* and *carbon fitting error* is small. Probably due to the assembling of a silane based polymer-framework just interacting weakly with the surface, both characteristics appear. The CSH-gel samples, treated or untreated, seem to represent characteristics of both surfaces. For the cement stone the high fitting error for the iOTES sample indicates a close degree of covering of the surface. The fitting error for carbon analysis is relatively high as well, but it has to be considered, that the silane alkylgroups do not represent a carbon surface as such. They just represent more the characteristics of a carbon than of a silica surface.

4 Conclusion: model of oligomer-size and distribution

With respect to the reaction rates, SSA and some geometric considerations, the oligomer size and distribution for PTES and iOTES on some mineral surfaces are described.

The tobermorite surface has no deprotonated silanol groups, so the silane-oligomers-surface interaction is weak. The fast polycondensation of the PTES leads to large silane oligomers, which develop before an interaction between silane-oligomers and surface takes place. Additionally the high SSA for the PTES-sample indicates the assembling of a discrete silane-polymer formed fragmentary at the surface. The N_2-molecules whilst the sorption experiments are sorbed at different sites on the accessible surface. The surface-characteristics influence the sorption-behaviour. In the case of the PTES-polymer the N_2-molecules are sorbed as well on the polymer as on the mineral surface and probe the more organic polymer and the silica surface. From these results it can be concluded, that the polymer doesn`t cover completely the pore surface.

For cement stone, the carbon-characteristics of the surface increase with increasing size of the alkylgroup of the silane. The coverage of the pore-surface with the iOTES-oligomers is closely-packed, don’t let the N_2-molecules pass to the original surface. The slower polycondensation of the iOTES could lead to the interaction with the surface of short oligomer chains which are more flexible. These smaller oligomer-chains can be arranged close together, patterning the original surface. The SSAs of the untreated and with iOTES treated samples are almost the same. This supports the assumption of a rather close, tight packing of the silane oligomer on the surface.

In Figure 5 a schematic view of the fragmentary packing of big PTES-oligomers (a) and the close packing of short iOTES-chains (b) on mineral surfaces is illustrated.

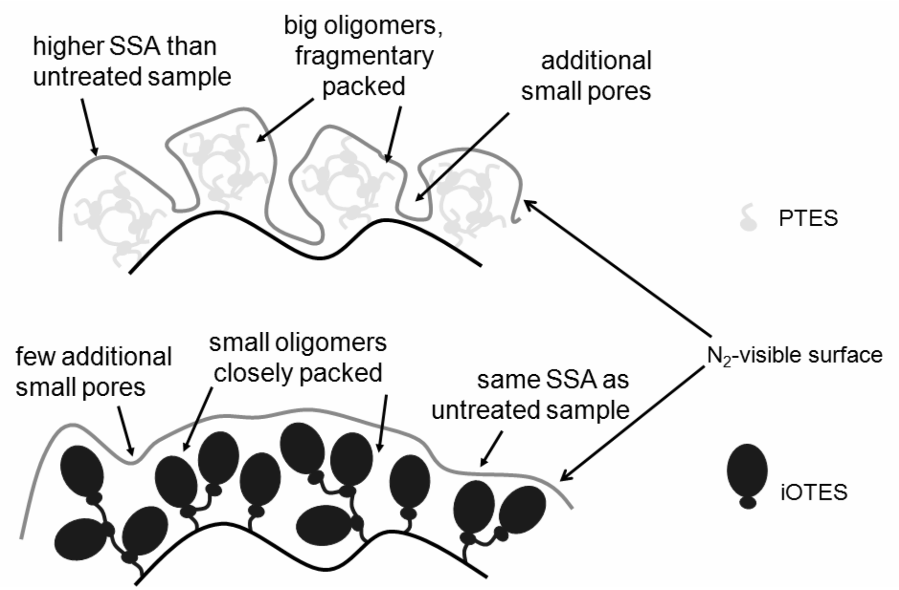

Figure 5: Schematic view of the oligomer packing for a) PTES and b) iOTES on mineral surfaces

The experimental data from the sorption-measurements analysed with NLDFT-methods combined with some energetic considerations from semi-empirical modelling of the silane condensation leads to a model of oligomer-size and -distribution on mineral surfaces.

References

[1] Georgi, U.: Funktionalisierte Gelschichten aus Tetraethoxysilanen und Alkyltriethoxysilanen, Dissertation, Freiburg, 7-13 (1993)

[2] Richardson, I. G.: The calcium silicate hydrates, Cement and Concrete Research (38) (2008) 137-158

[3] Oehmichen, D.: Mechanismen der Hydrophobierung zementgebundener Werkstoffe mit siliciumorganischen Verbindungen; Dissertation (2008) Universität Karlsruhe

[4] For an overview about computational chemistry see e.g. Jensen, F.: Introduction to computational chemistry, Wiley (1999) Chicester

[5] Brunauer, S., Emmett, P., and Teller, E.: Adsorption of Gases in Multimolecular Layers, J. Am. Chem. Soc., 60 (2) (1938) 309-319

[6] Sing, K. S. W.: Reporting physisorption data for gas/solid-systems with special reference to the determination of surface area and porosity; Pure & Appl. Chem. Vol. 57, No. 4, (1985) 603-619

[7] Thommes, M.: Recent Advances in the Physical Adsorption Characterization of Ordered and Amorphous Micro/Mesoporous Materials; Quantachrome Instruments (2005) Boynton Beach, Florida, USA

[8] Neimark, A. Ravikovitch, P.: Capillary condensation in MMS and pore structure characterisation; Microporous and Mesoporous Materials, 44-45 (2001) 697-707

[9] Powder Tech Note 36, Comments on the proper selection of adsorption or desorption branches for mesopore size analysis,

[10] http://www.micromeritics.com/Pressroom/Press-Release-List/Micromeritics-Releases-Six-New-NLDFT-Based-Models-for-Characterization-of-Carbon-and-Zeolites.aspx

[11] Spartan®: Wavefunction Inc.

[12] Herb, H. Gerdes, A.: TOF/MS for silicon based water repellents, Proceedings of Hydrophobe V – Fifth Int Conference on Water repellent treatment of building materials, De Clercq, H., Charola, A. E. (Hrsg.), Aedificatio Publishers, 2008, Freiburg 197-204