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Computational Chemistry to Investigate the Chemical Behaviour of Silanes and CSH –Gel

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Abstract

The chemical properties of cement based materials are, compared to morphology, and structure development, hardly described. However, the knowledge of the chemical characteristics is necessary to understand the processes taking place in cementitious materials in the presence of reactive compounds. The research focuses on the modification of the macroscopic properties of cement based materials induced by reactions at the molecular level. Detailed information about the chemical behaviour at this level will be helpful when deciding on the application of additives and could help to develop “tailor-made” chemicals for the construction industry. The study addresses the influence of the molecular structure of alkyltriethoxysilanes on their behaviour with the substrate. It is known that the hydration products of cement play an important role in the chemical reactivity of silanes and can not be considered an inert matrix. However, hydrated cement phases are extremely complex matter. Their structure at molecular level and their chemical properties are not fully understood. A novel approach to characterise their chemical properties is the application of inverse analysis. Using well-known chemical reactions, with the support of molecular modelling methods and computational chemistry, some advances can be made.

Keywords: computational chemistry, alkyltriethoxysilane, mineral surface, CSH-gel

1 Introduction

Cement based materials represent the most important material as the annual production of 2 billion tons of Portland cement per year shows. Therefore, much research was carried out to understand the characteristics of Portland cement and its hydration products. However, this was mainly focused on the characterisation of the structure and morphology of the hardened cement paste. But this knowledge does not necessarily help in understanding their chemical behaviour at a molecular level [1]. And this understanding is fundamental to gain an insight on how the hydrated cement paste reacts chemically. For example, the performance of construction chemicals, such as superplasticizers or silanes, depends upon their interaction with the cement clinker and hydration products, respectively [2]. A model which describes the chemical behaviour of these systems would be useful to develop effective construction chemicals in order to improve the performance of cement based building materials.

Previous studies have shown that there is a strong chemical interaction between silanes and cement based materials in which CSH-gel plays an active role [3]. Starting from this point, a new approach to describe the chemical behaviour of the CSH-gel has been developed. Experiments with water repellent agents indicate a strong influence of the type of alkyl group of alkyltriethxysilanes on their reactivity, i.e., kinetics of the reaction, penetration depth and the performance of the water repellent treatment [4]. Furthermore, it has been shown that the composition of the cement based materials (e.g. calcium hydroxide content, types of aggregates) influences the kinetics of the silane reaction. To explain these phenomena the reaction mechanisms need to be clarified at a molecular level. For this purpose, the newly developed computational chemistry methods are very helpful. With these methods molecular surfaces, molecule orbitals and energy levels of complex molecules such as silanes, silanols and polysiloxanes can be calculated and presented in a comparable and visually comprehensible way. The calculated data can be used to formulate hypotheses for the chemical mechanisms that determine film formation with the single steps hydrolysis, condensation and binding to the surface of the solid.

The objective of this research work is the modelling of the chemical reactions between silanes and cement based materials by means of computational chemistry. With this model it should be possible to optimize the structures of silanes at the molecular level so as to improve the performance of water repellent agents applied to concrete structures in practice. In this paper the first results of these investigations are presented and discussed.

Table 1: Survey of methods of molecular modelling

<table>
<tr><th colspan="5">Computational Chemistry</th></tr>
<tr><th>Molecular Dynamic Methods</th><th colspan="2">Force Field Methods</th><th colspan="2">Quantum Mechanical Methods</th></tr>
<tr><td>Simulation of the motion of a large number of molecules. Single molecules are modelled with force field or quantum mechanical methods.</td><td colspan="2">Simulation of one (huge) molecule. Base are classical physics (bonding between two atoms is described with spring constants</td><td colspan="2">Base is the Schrödinger equation (unsolvable for many particle systems), diverse methods use different approximations and simplifications</td></tr>
<tr><td colspan="5">Approximations:
Born-Oppenheimer-approximation: because of the bigger mass of the nuclei, the electrons move independently
Hartree-Fock-approximation: instead of many dependent electrons in one equation, independent particles in many equations</td></tr>
<tr><th>Density Functional Methods</th><th>Semi-empirical Methods</th><th colspan="3">ab initio Methods</th></tr>
<tr><td rowspan="3">Energy of a system as a functon of electron density</td><td rowspan="3">Directly from Hartree-Fock equations
Discrimination of valence- and core- electrons
Neglect of overlap of different atomic orbitals
Experimental parameters involved</td><td>Hartree-Fock Method</td><td></td></tr>
<tr><td rowspan="2">Directly from the HF-equations with different basis sets</td><td>Correlated Methods</td></tr>
<tr><td>Correlation of electrons is involved again
(Configuration-interaction-, Coupled-Cluster-, Perturbational Methods</td></tr>
</table>

2 Molecular modelling

2.1 Fundamentals

The field of computational chemistry increases with the progress in computational technology. In Table 1 the most important aspects of these models are summarized. The first were the force field models, based on the laws of classical physics, where bonding between the atoms in a molecule is considered as a spring and the bonding strength is calculated

using spring constants. These models allow describing complex molecules and their configuration, but they can not predict chemical reactions.

For the calculation of parameters determining chemical reactions, i.e., bonding energy, dissociation energy, energy of molecular orbitals, models based on quantum chemistry methods are necessary. The fundamentals of these methods are based on the Schrödinger-equation, which is analytically unsolvable. Therefore, two approximations are needed to deal with this problem. One is the Born-Oppenheimer-approximation, which separates the nuclei-motion from the electron-motion, so that the nuclei can be regarded as fixed due to their bigger mass. The second is the Hartree-Fock-approximation that derives a multitude of independent-particle-problems from a dependent-many-particle-problem. This means that each electron is calculated in a field representing the average of all other electrons. In this way the complex behaviour of the real molecule can be simplified and becomes a mathematically solvable problem. Depending on different factors, such as the capacity of the computer system, molecule type and size, several quantum mechanical methods are used, briefly described in the following paragraphs. Details about these methods are given elsewhere [5].

- **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. Presently the models can handle large molecules since the mathematics behind them are relatively simple.
- **Ab initio methods** use only defined approximations and physical constants. First, Hartree-Fock-equations are formulated for each atom. Due to the fact that in the Hartree-Fock-approximation (division in many one-particle-problems) the correlation of electrons is not included, further approaches have been developed leading to correlated methods. High capacity computers are required as the mathematics behind these models are very complex. Basically they introduce excited states with virtual orbitals from the Hartree-Fock calculation to calculate molecules in vibration or in fields. Therefore, a higher flexibility of the description of the electron distribution is possible that allows electrons to avoid each other [6].
- **The density functional method** calculates the energy of a system as a 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.

Nucleophilic substitutions (S_N–reaction) can be modelled with Hartree-Fock-methods. Since polycondensation of alkyltriethoxysilanes is also a S_N–reaction, computer software suitable for the modelling of these

reaction types was chosen to investigate the chemical behaviour of selected silanes. The results of these first calculations have been compared with experimental observations.

2.2 Application of computational chemistry methods

In the last years, many applications of molecular modelling were developed for biochemistry in general and for pharmacy in particular to avoid expensive and extensive experimental work [7-9]. On the basis of their successful applications, these methods have been used in other areas as well, e.g., development of nano-materials, additives, polymers and catalysts. In these fields different results are needed so certain strategies were developed. For molecules with thousands of atoms mostly force field methods or semi-empirical methods were adopted. With quantum-mechanical methods information on the characteristics of chemical reactions and thermodynamical data can be done. However, the quality of the calculated data will depend on the size of the investigated molecule, since the computational cost increases significantly with molecule size. For the investigation of really large systems, e.g., proteins, where mostly special binding sites are observed, hybrid procedures were developed, which allow the combination of the force field- and quantum-mechanical-methods [5].

The pioneering pharmaceutical field has developed models for a multitude of compounds avoiding costly and time consuming testing procedures. Provided that the biological effect and the target molecule are known, computational chemistry can be used to develop and optimise a pharmaceutical profile.

Even in geochemistry efforts are being made to describe complex systems consisting of different minerals and aqueous solutions using computational chemistry. These applications require a really high computer capacity. The first simulations were performed with force field methods [10]. In addition semi-empirical computation in the field of chemical reactivity such as the handling of incorporated metal ions in a lattice was established [11]. With the development of the density functional theory a promising tool is available for further calculations.

Computational approximations to the structure of bulk liquid water in cementitious materials were carried out with special molecular dynamic methods, such as the CLAYFF force field method [12]. To clarify the molecular structure, diffusive dynamics and hydration enthalpy of adsorbed water were simulated for brucite, gibbsite, hydrotalcite, muscovite and talc substrates. Close relationships between the substrate structure and the structure, dynamics and energetics of water at mineral surfaces have been reported [13]. The structures within and near the boundary layers are important for the analysis of the interactions of water and dissolved ions with oxide and hydroxide surfaces. For non-crystalline systems, such as the CSH-gel, these data are often unavailable or hard to

access. However, this currently ongoing work may lead to simulations that would allow their application to cement materials [14].

The present research project models the interaction between the solid (e.g. quartz, CSH-gel) and different silanes such as iso- and n-octyltriethoxysilane and calculations are already in progress.

3 Polycondensation of alkyltriethoxysilanes

The polycondensation of alkyltriethoxysilanes is a nucleophilic substitution. The reaction can be subdivided into two reaction steps, first the hydrolysis, followed by the condensation. For tetraethoxysilane and different alkyltriethoxysilanes both reactions, that can take place in either acid or alkaline environments, were examined in detail. Figure 1 shows both reactions which can proceed simultaneously and competitively [15, 16].

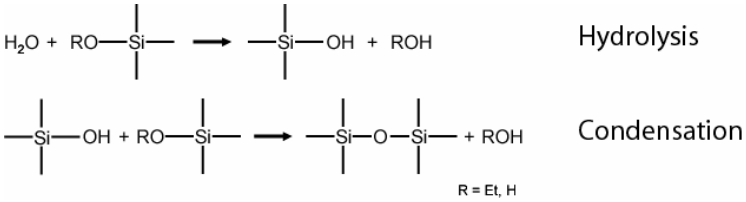

Figure 1: Reactions of alkyltriethoxysilane in an aqueous environment

The polycondensation of the alkyltriethoxysilanes is strongly influenced by factors such as concentration, pH and temperature. It results in the formation of polymers having different properties, such as specific surface, pores and density. The reaction rate of the alkyltriethoxysilanes decreases with increasing alkyl group chain length. In an alkaline environment the attack of a deprotonized silanol on a hydrolysed compound is the rate determining step for polycondensation. The acidity of the OH-groups increases with the increasing polycondensated siloxane. For this reason the condensation of large siloxanes occurs preferentially with monomers [15].

4 Results and discussion

First the different steps in the polycondensation for different types of alkyltriethoxysilanes were investigated. For this purpose, a software-package, Spartan™ [17] was used. It can be used to calculate single molecules in the gaseous phase with different approaches such as quantum mechanical as well as force field methods. For larger systems, two force fields can be implemented and four different semi-empirical

calculations can be carried out. Hartree-Fock-, density-functional- and correlated methods (perturbational- and configuration-interaction calculations) with several basis sets are also available.

These first calculations were to analyse the influence of the chemical structure of silanes on the basic reactions (hydrolysis and condensation). The calculations for the monomers were carried out with the Hartree-Fock-method and a 6-31G(d, p) basis set considering that a certain diffuseness and angular flexibility can be obtained [18-20]. Since with the Spartan™ software, processes in solution or solid state can not be computed and the computational correlated methods are too expensive, only qualitative comparisons were carried out and no quantitative statements could be formulated.

Experimental results from laboratory studies and case studies have shown the different behaviour of the alkyltriethoxysilanes used as water repellent agents, e.g., [21]. Making use of this data, the study examined in detail the behaviour of n-propyltriethoxysilane (n-PTS) and iso-octyltriethoxysilane (i-OTS).

The hydrolysis of n-PTS is characterised by the very fast ethanol-release compared to that of i-OTS. In the presence of hardened cement paste almost 90% of the theoretical amount of ethanol for complete hydrolysis is released after 2 h. For i-OTS only 77% of the theoretical amount of ethanol is detected after 7 days [21].

To elucidate the causes for this difference, the so-called Lowest Unoccupied Molecular Orbital, (LUMO) is calculated, because hydrolysis of the alkyltriethoxysilane involves a nucleophilic attack by a hydroxyl ion. The favoured orbital for this attack is the LUMO and the best area is positive polarised. Hence, the molecular surface with the electrostatic potential is calculated and, in addition, the molecular surface shows the shape of the molecule in a more realistic way.

Figure 2 illustrates a visualisation of the LUMO and molecular surface for n-PTS and i-OTS resulting from theoretical calculations for single molecules in the gaseous phase. For the case of n-PTS, two parts of the LUMO show a theoretical opportunity for interactions. One of these is located at the right hand side of the molecule. On the contrary, i-OTS shows just one LUMO area and this is hidden in a fold of the molecular surface. That means that the octyl group hinders the attack of another molecule and leads to a slower ethanol release rate as compared to n-PTS. The results show clearly the influence of the chemical structure of the silanes on the chemical reactivity and give some helpful information which can be used to explain the performance of water repellent agents in practice.

If the computations for the molecules in alkaline solutions deliver analogue results, the differences in the reaction rates could be explained by the shape of the LUMO areas and that of the molecule surface.

The following step is the polycondensation leading to the formation of a polysiloxane film which is absorbed on the inner surface of the capillaries.

So far there is a lack of understanding regarding the chemical structure of the polysiloxane films attached to the cementitious matrix. Therefore, this topic was also investigated and is reported in this volume [22, 23].

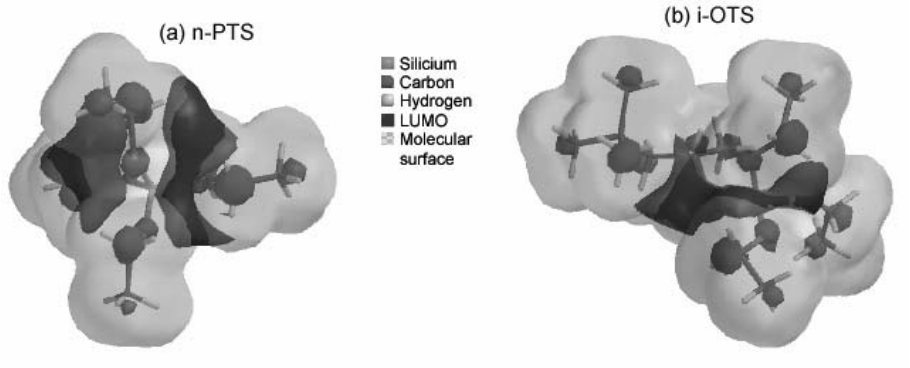

Figure 2: Visualisation of the LUMO and molecular surface resulting from theoretical calculations by HF//6-31G(d,p) for (a) n-PTS and (b) i-OTS

For the investigation of the chemical structure of the polysiloxane film a special mass spectrometry technique called MALDI-TOF/MS (Matrix Assisted Laser Desorption Ionization – Time of Flight – Mass Spectrometry) was used. Compared to conventional ionisation methods where large organic molecules are fragmented, this method allows the analysis of high molecular weight organic molecules and polymers.

For use with MALDI, the sample to be analysed, is co-crystallised with a matrix and the matrix/sample-crystal is vaporised with special lasers. This leads to a plume of excited and ionised molecules. In this case a sodium ion of the matrix molecules is added to a sample molecule to produce a charged ion. The exact mechanisms for this are not fully understood. The ionised compounds are analysed with a mass spectrometer using a TOF-detector. Further details of this method are given in [24, 25].

While research on i-OTS is in progress, the type of siloxane compounds resulting from the polymerisation of n-octyltriethoxysilane, n-OTS, in an alkaline solution were identified by means of the MALDI-TOF/MS. The results reveal that the main reaction product is $T_7(OH)_3$, where T= $C_8H_{17}Si$ [26].

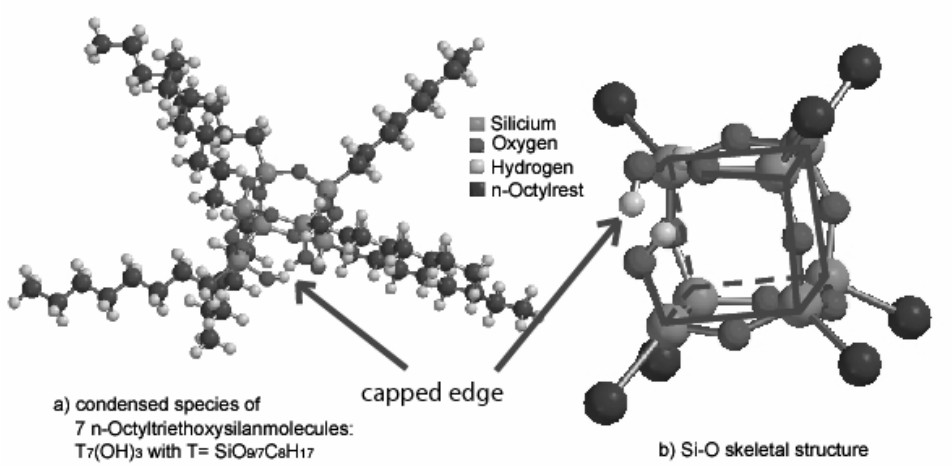

Figure 3: Molecular structure of $T_7(OH)_3$ (a) and its Si-O-skeletal cubic structure (b) in which the octyl groups are presented as big dark spheres.

With the help of Spartan™ the structure of the $T_7(OH)_3$ was calculated. The skeletal structure of this oligomeric siloxane is a cube with a capped edge as shown in Figure 4. Conceivably this molecule would connect to the mineral surface at this edge. But the chemical reaction that leads to the formation of this molecule takes place in an alkaline solution while in reality it takes place in the presence of a solid matrix (e.g CSH-gel). Hence, it can be expected that the formation as well as the bonding of the polysiloxane film will be influenced by the nature of the solid and by the presence of terminal OH-groups on the CSH gel, in particular. This assumption is supported by the results obtained with density functional methods regarding the adsorption of alkyltriethoxysilanes at a tridymite-surface. The results showed the formation of covalent Si-O-Si bonds as well as hydrogen bonds at the alkyl chain during polycondensation [18-20]. The analyses of the reaction products formed in the presence of CSH-gel will give detailed information about the polysiloxane structure and the specific reaction mechanisms for the different silanes.

The analysis of these chemical reactions will lead to the assessment of the role of the CSH-gel in the polycondensation of silanes. Furthermore, by inverse analyses of various chemical reactions between CSH-gel and organic chemicals the modelling of the chemical properties of cement-based materials in general will be possible. This is of great importance for the targeted modification of silanes to improve their performance and durability and will be helpful to design more effective chemicals for the construction industry.

5 Conclusions and outlook

From the results presented here the following conclusions can be drawn:

- The methods of molecular modelling and computational chemistry are powerful tools for the analyses of chemical reactions that take place between silicon organic compounds and cementitious materials.
- The differences in the chemical reactivity of propyltriethoxysilane and iso-octyltriethoxysilane can be explained by the properties of the molecules such as energy and geometry of the molecular orbitals.
- Density functional methods are necessary for computing the bonding or absorption of silanols and polysiloxanes to the mineral surface.
- Reactive chemical compounds react in a characteristic way with cementitious materials. Hence, clarifying these reaction mechanisms will also help to characterise the chemical properties of the cementitious materials. If the chemical reactions can be described completely at the molecular level, reactive compounds can be used as “chemical sensors” to identify the chemical properties of the hydrated phases in the latter materials, since these are difficult to assess with other methods.
- For all works with computational methods it is essential to corroborate the results of the calculations with experimental data.

References

[1] G. Constantinides and F.-J.Ulm, The nanogranular nature of C–S–H, Journal of the Mechanics and Physics of Solids (55) (2007) 64–90.

[2] Plank J., Dai, Z. and Andres, P.R., Preparation and characterization of new Ca–Al–polycarboxylate layered double hydroxides, Materials Letters, (60) (2006), 3614-3617

[3] D. Oehmichen, R.Nüesch und A. Gerdes: Inverse Chromatographie - Chemische Reaktionen an zementgebundenen Werkstoffen, in: GDCh-Fachgruppe Bauchemie (Hrsg.), Tagung Bauchemie, Berlin (2005) 181-191

[4] Oehmichen, D., Reaktiver Transport siliciumorganischer Verbindungen in porösen zementgebundenen Werkstoffen, Forschungsbericht, Forschungszentrum Karlsruhe, in preparation

[5] http://www.chemgapedia.de/vsegine/tra/vsc/de/ch/trajektorien/modelling.tra.html

[6] Rode, B. M., Hofer, T. S., Kugler, M. D.: the basics of theoretical and computational chemistry; Wiley-VCH, Weinheim (2007)

[7] http://www.fz-juelich.de/compchem/proceedings/Boehm/boehm.html

[8] Kubinyi, H.: Der Wandel in der Arzneimittelforschung – vom glücklichen Zufall zum gezielten Entwurf, Informationen des Vereins „Forschung für Leben“ (Nr 59) (April 2001)

[9] Böhm, H.-J.; Klebe, G.; and Kubinyi, H.; Wirkstoffdesign; Spektrum Akademischer Verlag GmbH; Heidelberg (1996)

[10] Kubicki, J.D., Bleam,J.F.: An introduction to molecular modeling; Molecular modeling of clays and mineral surfaces, CMS workshop lectures, Volume 12, The Clay Mineral Society (2003) 1-25

[11] Skipper, N. T.: Monte Carlo and molecular dynamics computer simulation of aqueious interlayer fluids in clays; Molecular modeling of clays and mineral surfaces, CMS workshop lectures, Volume 12, The Clay Mineral Society (2003) 102-142

[12] Kalinichev, A., Kirkpatrick, R.: Molecular dynamics modeling of chloride binding to the surface of calcium hydroxide, hydrated calcium aluminate and calcium silicate phases; Chemical Materials (14) (2002) 3539-3549.

[13] Wang, J., Kalinichev, A., Kirkpatrick, R.: Effects of substrate structure and composition on the structure, dynamics and energetics of water at mineral surfaces: A molecular dynamics modeling study; Geochimica et Cosmochimica Acta (70) (2006) 562-582

[14] Kalinichev, A., Wang, J., Kirkpatrick, R.: Molecular dynamics modeling of the structure, dynamics and energetics of mineral-water interfaces: application to cement materials; Cement and Concrete Research (37) (2007) 337-347

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

[16] N. Söger: Hydrolytische Darstellung, Stabilisierung und massenspektroskopische Charakterisierung von Siloxanen und Siloxanolen, Dissertation, Hannover, 1-21 (2002)

[17] Spartan: Spartan ’06 Wavefunction Inc., Version 2006 für Windows

[18] A. Dkhissi et al.: Chemical Physics (323) (2006) 179-184

[19] A. Estève et al.: Computatonal Materials Science (33) (2005) 282-286

[20] A. Dkhissi et al.:Chemical Physics Letters (400) (2004) 353-356

[21] D. Oehmichen, A. Gerdes und A. Wefer-Röhl: Reaktiver Transport in zementgebundenen Werkstoffen – Neue Lösungen für alte Probleme, in: GDCh- Fachgruppe Bauchemie (Hrsg.), Tagung Bauchemie, Siegen, 165-174 (2007)

[22] H. Herb, A. Gerdes: TOF/MS for characterization of silicon-based water repellents, proceedings Hydrophobe V (2008)

[23] D. S. Oehmichen, A. Gerdes and A. Wefer-Roehl, Reactive Transport of Silanes in Cement based Materials, Proceedings Hydrophobe V (2008)

[24] H. Pasch and W. Schrepp, MALDI-TOF Mass Spectrometry of Synthetic Polymers, Springer-Verlag, Berlin (2003)

[25] Karas, M. et al.: Matrix-Assisted Ultraviolett Laser Desorption of non-volatile Compounds; International Journal of Mass Spectrometry and Ion Processes, (78) (1987) 53-68

[26] H. Herb und G. Brenner-Weiß: MALDI-TOF/MS zur Charakterisierung von siliziumorganischen Hydrophobierungsmitteln, in: GDCh- Fachgruppe Bauchemie (Hrsg.), Tagung Bauchemie, Siegen, 359-364 (2007)