Performance Oriented Functionalisation of Concrete: An Integrated Approach for Prevention in Construction

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ABSTRACT

The long-term preservation and the future-oriented development of the infrastructure are of utmost importance for every country in the world. An increasing failure of infrastructure underpins a tremendous need for action. The reasons for this unsatisfactory situation are various, but certainly among them is often an insufficient performance of the building materials. This holds particularly true for reinforced concrete and its additives, which are nowadays commonly developed by empirical research. Almost all shortcomings of concrete durability are related to the transport of detrimental substances into the pore system. In this regard, a promising approach to prevent chemical deterioration processes is a functionalisation of the pore system by means of organosilicon-based surface treatments in order to hamper the uptake of aggressive aqueous solutions. However, little is known about the reaction mechanisms and the nature of the reaction products associated with such measures. However, this is necessary to obtain reliable information about their performance and ideally to develop these technologies further in a more target-oriented manner. The insufficient understanding of these processes has its origins in the inability of investigations of the reaction course of silicon organic compounds in the pore structure of cement-based systems and their underlying physical and chemical principles. This applies in particular to film-forming reactions in alkaline environments of the pore structure, which lead to functionalization (e.g. hydrophobic effect). The approach of this study is therefore to investigate the reaction products in model systems using mass spectrometry and to explain the course of the reaction by means of computational chemistry. In this way, reaction products of different reaction steps of the condensation of specific components into larger oligomers were characterized and the reaction sequence was explained by molecular modelling. These results contribute to a deeper understanding of the reactions and types of reaction products of organosilicon compounds used to improve the properties of cement-bound materials. This promotes further steps towards the performance-oriented development of such surface protection technologies.

Keywords: durability of concrete, computational chemistry, water repellent treatment, silanes.

1.0   INTRODUCTION

1.1   Background

Maximizing the service life of infrastructure constructions is an important issue with substantial impact on the competitive position of a nation. In particular, the protection of concrete constructions represents a major challenge as they show often a low sturdiness during use, especially if they are subjected to aggressive aqueous environments. In this regard, the functionalisation by means of water-repellent agents are common measures. Establishing hydrophobic properties of the mineral surfaces can be performed by means of silicon organic compounds.

However, lessons learned from practice indicate that the current state-of-the-art of such surface protection systems is often insufficient to ensure long-term protection of the buildings, especially in view of the required service life in the order of several decades. Therefore, the durability of such measures in terms of chemical stability and long-term effectiveness is still debatable and subject of intensive research activities addressing particularly the various application fields of concrete (e.g. Schueremans, 2007 and Christodoulou, 2013).

Targeting a performance oriented development of a chemical functionalisation of mineral materials, a fundamental understanding of the chemistry of the functionalising agents and furthermore their interactions with the mineral substrates is required.
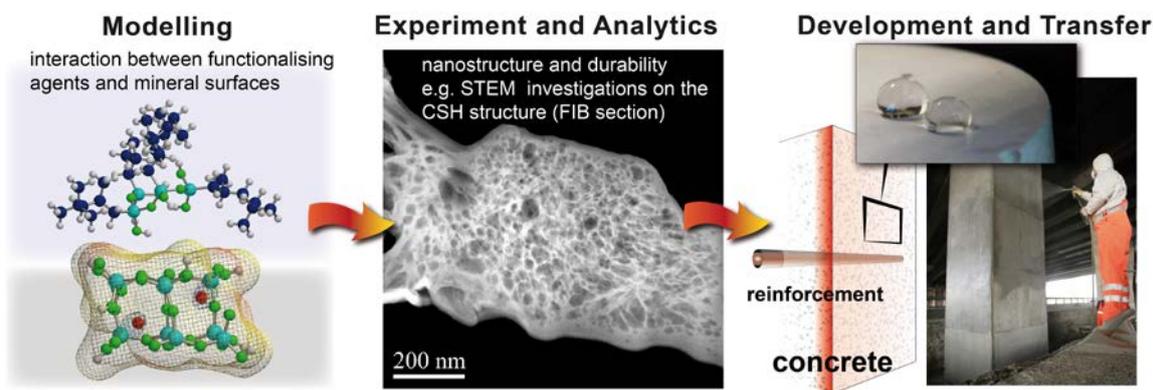
Fig. 1. Approach for the development of advanced surface protection technologies for concrete
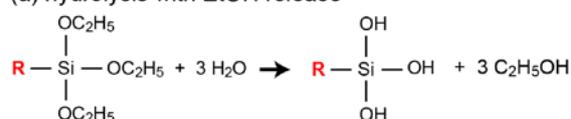
In particular regarding the hydrophobisation of cement-based materials with organosilicon compounds as alkyltriethoxysilanes (ATES), very little is known about the reactions that build up the hydrophobic properties of the cement paste. In order to promote substantial innovation in this area, a research project has been launched to decipher the mechanisms of the development of the hydrophobic effect in cement-based systems. Therefore, a research activity was started to unravel precisely the mechanisms underlying the hydrophobic effect of ATES in cementitious systems. The project concept integrates computational chemistry and experimental investigations of the surface chemistry of relevant mineral compounds in order to enable a development activities to improve performance of the functionalisation of cement-based materials (Fig. 1).

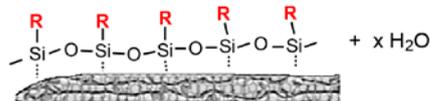## 1.2   Polycondensation of Alkyltriethoxysilanes

In general, the reactions that take place with ATES when applied to cement-based materials can be seen as a complex interplay of chemical reactions and transport processes. The two processes influence each other. In the alkaline environment of the pore system of cement-based materials, the reaction of ATES, which furnishes the pore structure with water-repellent properties, can be understood as a two-stage reaction of hydrolysis and condensation. This so-called polycondensation of ATES in the presence of cement paste is shown schematically in Fig. 2. The initial hydrolysis reaction with an release of Ethanol (EtOH), as shown in Fig. 2a, is followed by condensation step, resulting in the formation of larger oligomers that may further create links to mineral surfaces and thus change the surface properties of these substrates (Fig. 2b).

Both are nucleophilic substitutions and proceed depending on reaction conditions simultaneously and competitively. The tendency for nucleophilic attacks at the Si-atom increases; the more electron-pulling groups are attached, as indicated by the blue arrow in Fig. 2c.
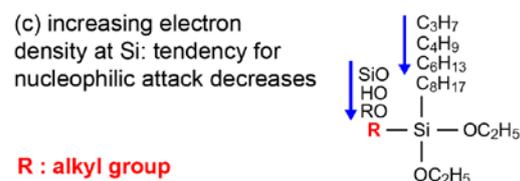

Fig. 2. Reaction steps of the polycondensation of ATES: hydrolysis (a) and condensation (b) of the polycondensation of ATES, and tendencies for nucleophilic attacks of alkylalkoxysilanes (c)

The polycondensation of ATES is strongly affected by factors as chemical structure, concentration present in the reaction solution, and the hydro-chemical conditions (e.g. pH and temperature). The reaction rate of ATES decreases with increasing chain length of the alkyl groups. In alkaline environments, the attack of a deprotonated silanol on a hydrolysed compound represents the rate determining step for the polycondensation. Furthermore, the acidity of OH groups increases with increasing silane oligomer size. Therefore, the condensation of silane oligomers occurs preferentially combining monomers (Brinker and Scherer, 1990, and Georgi, 1998).

These compounds tend to form larger units that may further result in hydrophobic polymer films, creating consequently hydrophobic properties in the pore structure of the cement paste. However, the reaction steps are strongly influenced by a huge variety of factors, as the structure of the molecule and the physical and hydro chemical conditions in the aqueous environment. In particular, in view of the

material behaviour in practice, it appears mandatory to understand the most relevant interrelationships. However, only a few specific aspects of this reaction sequence are well known or have been proven experimentally. For example, regarding the reaction rate Oehmichen, 2008, was able to experimentally demonstrate that the release rate of ethanol is significantly influenced by the presence of mineral surfaces. This indicates, that type and as well state of the concrete are of relevance for the reaction and may in turn affect the performance of an application in practice. Furthermore, Herb, 2015 showed that the use of advanced mass spectrometry is suitable for the analytical monitoring of certain reaction processes. Nevertheless, a comprehensive experimental characterization of these reaction mechanisms is only feasible to a very limited extent. Neither the chemical properties of a CSH-gel, the most important constituent of hardened cement paste nor the exact reaction mechanism of the ATES are known. In order to decipher the reaction steps, approaches of computational chemistry are therefore required.

In this contribution, relevant molecular processes have been investigated applying theoretical methods and then compared with experimental results. Explanatory approaches regarding the reaction rate are derived from computation of the charge distributions within the molecules. In addition, the intermediates in the formation process of polymer films have been characterized applying mass spectrometry on model systems, e.g. observing the condensation products of ATES in pure alkaline solutions. Moreover, the semi-empirical modelling provides relevant details of the oligomer constitution and contributes as well to a profound understanding of the reaction mechanisms paving the path to a performance oriented development of functionalising agents for cement-based construction materials.

2.0 METHODS

2.1 Computational chemistry

In this study tools of computational chemistry are used to contribute to the detailed clarification of chemical reactions, in particular of silicon organic compounds, which are experimentally inaccessible. These tools bass upon quantum mechanical concepts. Fundamental of all quantum mechanical methods is the so-called Schrödinger equation, which is analytically unsolvable. One of the main issue of all modelling methods is the calculation of the electron correlation, this means the dependence of the energy of each single electron of all others at any point of time. To solve these problems the different modelling methods use different ways to approximate the exact solution of the wave function. In the present study *semi-empirical* and *density functional theory methods (DFT)* have been applied.

Molecular charge distribution by means of DFT

By means of DFT methods, the energy of a system as function of the electron density will be calculated. Thus, the DFT can be used to calculate the electrostatic potential from the charge distribution. With the used software (ADF from Scientific Computing and Modelling, SCM, Amsterdam), this calculations were performed in three distinct steps. Initially, the total density is split off into atomic densities. The atomic densities are used to define atomic multipoles. Then the atomic multipoles are reflected through an exact distribution of charges over all atoms. This method delivers MDC-q-values, which reproduce the atomic charges in a better way than other methods (Swart *et al.*, 2001).

For the calculation of the electrostatic potential of the monomers the geometries of the alkyltriethoxy-, alkyldiethoxy-, alkylmonoethoxy- and alkyltrihydroxy-silane formed during the hydrolysis are optimised. For this procedure a generalised gradient approximation, GGA, functional (PW91) and a split valence basis set with polarization functions (TZ2P) are used.

Semi-empirical modelling

The *semi-empirical methods* use experimentally 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 for parameterized atoms good results.

For the semi-empirical modelling, the "Spartan"-software from Wavefunction Inc. is used. One of the methods is PM3, a widespread method for a multitude of compounds. It contains almost all atoms with a broad statistical founded parameterization. It is suitable for the modelling of molecular geometries and even for hydrogen bonds, which are problematic for some other methods like AM1 (Hehre, 2006). The semi-empirical modelling is used to obtain the energies of a set of atoms, along the reaction path (step S1 to step 12b) whilst the constitution of the oligomers. The sum of Si-, O-, C- and H-atoms in the sets is the same (Table 1). The calculated values for energies are given in atomic units (hartrees), au, 1 au = 2625 kJ/mol (Hehre, 2006).

2.2 Mass spectrometry

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

Table 1. Set of atoms for the reaction steps whilst the constitution of the oligomers, starting from eight ATES-monomers in the presence of 26 water molecules

Step	Oligomer	H_2O	Set of silanes with propyl-group (PTES)				Set of silanes with isobutyl-group (iBTES)				Set of silanes with isooctyl-group (iOTES)			
			Si	O	C	H	Si	O	C	H	Si	O	C	H
S1	monomers	26	8	50	24	132	8	50	32	148	8	50	64	212
S2	dimer	27	8	50	24	132	8	50	32	148	8	50	64	212
S3	trimer	28	8	50	24	132	8	50	32	148	8	50	64	212
S4	tetramer	29	8	50	24	132	8	50	32	148	8	50	64	212
S5	tetramer (1ring)	30	8	50	24	132	8	50	32	148	8	50	64	212
S6	pentamer	31	8	50	24	132	8	50	32	148	8	50	64	212
S7	hexamer	32	8	50	24	132	8	50	32	148	8	50	64	212
S8	hexamer (2rings)	33	8	50	24	132	8	50	32	148	8	50	64	212
S9	heptamer	34	8	50	24	132	8	50	32	148	8	50	64	212
S10	heptamer (3rings)	35	8	50	24	132	8	50	32	148	8	50	64	212
S11a	heptamer (4rings)	36	8	50	24	132	8	50	32	148	8	50	64	212
S11b	octamer	36	8	50	24	132	8	50	32	148	8	50	64	212
S12b	octamer (4rings)	37	8	50	24	132	8	50	32	148	8	50	64	212

Practically, an aqueous solution of sodium hydroxide (NaOH) and tetrahydrofuran was used to simulate the alkaline environment of cementitious materials without any interference of solid matrix like sorption or transport effects. For the reaction 100 µL of the appropriate silane were dissolved in 300 µL tetrahydrofuran and 28 µL of aqueous NaOH solution were introduced in a 2 ml PE tube. The mixture was stirred at room temperature for 7 days. After this procedure, samples were taken and diluted with tetrahydrofuran (1:100) for the investigation by means MALDI-TOF/MS. As well, samples without silane have been measured as a reference. For application of the MALDI technique, the sample was co-crystallised with a matrix. Further, the matrix/sample-crystal was vaporised with by means of lasers, generating a plume of excited and ionised molecules. The ionized compounds are analysed with the mass spectrometer equipped a TOF-detector. Further details of this method are given in Pasch and Schrepp, 2003 or Karas *et al.*, 1987, repectively.

3.0 RESULTS AND DISCUSSION

3.1 Determination of the oligomer distribution

Figure 3 shows the results for the investigation of the oligomer distribution by means of MALDI/TOF-MS for the experiments with PTES, iso-butyltriethoxysilane (iBTES), and iOTES. For these three ATES a similar distribution was revealed. Surprisingly, the main product is the same for the three different ATES. It is an oligomer of the constitution $T7O_2(OH)_3$, with $T=SiC_nH_{2n+1}$. For PTES, a T8-oligomer cannot be detected, but for iBTES and iOTES in small amounts.
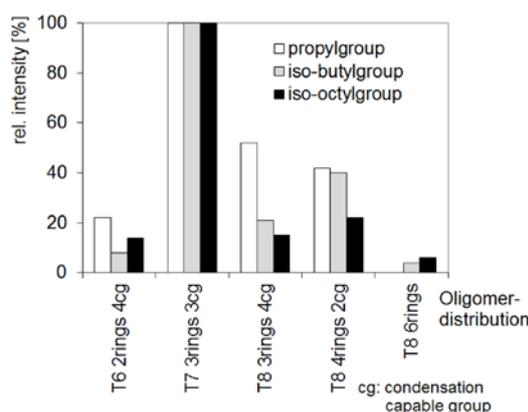
Fig. 3. Distribution of oligomers from MALDI/TOF-MS-experiments in pure alkaline solutions

3.2 Calculation of the atomic charges

The calculated atomic charges of Si for these monomers are given in Fig. 4. It is apparent that the atomic charge at the Si atom increases with increasing degree of hydrolysis for all silanes independent of the alkyl groups. The Si atoms of triethoxysilanes have the lowest atomic charge and the trihydroxysilanes have the highest atomic charge. When compared to iBTES and iOTES at each stage of hydrolysis, the Si of the PTES shows up the highest atomic charge. These results explain the difference in the reactivity of the different ATES found in experimental studies reported e.g. by Oehmichen, 2008. For PTES the ethanol release in pure alkaline solution proceeds at 97% in one hour. In contrast to that, in the comparable experiment with iOTES the amount of ethanol reached a value of 98% after a time span of 198h. Thus, this type of calculation appears suitable to predict the behaviour of other organosilicon compounds.
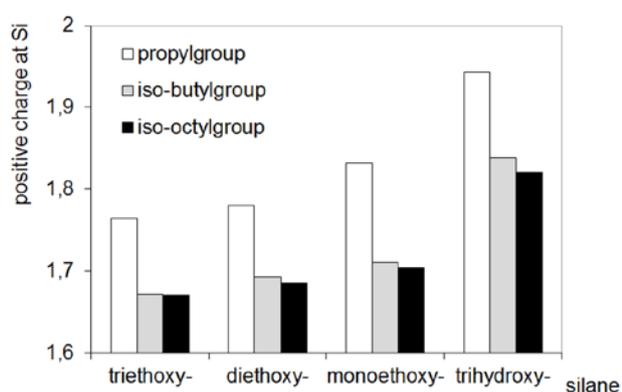
Fig. 4. Computed positive charge at Si from MDC-q calculations

3.3 Calculation of the oligomer constitution

Due to the chemical structure (three alkoxy groups) of the silanes the polycondensation leads via dimers and trimers to the formation of tetramers which can occur as chains (S4) or rings (S5). An important step in the constitution of oligomers is therefore the formation of the four-membered ring. The ring closure leads to four different configuration isomers, aaaa, aaab, aabb, and abab. In Fig. 5 for PTES as an example, the four possible isomers are shown in the first column, the sets of step S4 in the second column, and the sets of step S5 in the third column. Conversions are only possible, if a ring-bond is broken. Hence, if the ring is closed and the condensation proceeds, the ring has a strong influence on the geometry of the final product, which is shown.

For all the silanes studied, the calculated energy of the sets containing the four possible isomers for a four-membered ring and the situation immediately before the ring closure is calculated with 30 or 29 water molecules, respectively. The number of atoms in all sets is the same for silanes with the same alkyl group (Table 1). Each set of all steps for each ATES is geometry optimized applying a semi-empirical method (PM3). The energy from the optimized geometry its obtained and the computed results are shown in Table 2. The value of the energy is the lowest for the set of step S5 for the aaaa-isomer formed from PTES, and for the abab-isomers formed from iBTES and iOTES. If the sets of step S4 are considered, the value of the energy for the sets leading to the aaab-isomer represent the lowest for all three ATES. The corresponding values are printed in bold type in Table 2.

In further calculations, energy values in au were calculated for the products resulting from the progressive polycondensation of eight tri-hydroxysilane monomers and 26 water molecules (S6 to S12b) (Table 3). In each step, a Si-O-Si bond is established by releasing a water molecule. The set is geometry-optimized with PM3. For the isobutyl and iso-octylsilane systems, the propyl silane sets

are copied and the alkyl groups are enlarged in order to obtain a similar arrangement of the molecules, in particular the water molecules and the hydrogen bonds. The geometries of the result sets are then optimized.

Table 2. Semi-empirical (PM3) determined energies of the tetramer chains before ring closure (second column in Fig. 5) to different configuration-isomers

| | Energy of the chain before the ring closure (au) | | |
	propyl	ibutyl	ioctyl
aaaa	-4.2168	-4.2435	-4.3767
aaab	**-4.2320**	**-4.2579**	**-4.3910**
aabb	-4.2187	-4.2550	-4.3757
abab	-4.2262	-4.2457	-4.3883
	Energy of the ring isomers (au)		
	propyl	ibutyl	ioctyl
aaaa	**-4.2284**	-4.2598	-4.3849
aaab	-4.2145	-4.2541	-4.3899
aabb	-4.2274	-4.2526	-4.3797
abab	-4.2195	**-4.2633**	**-4.3956**

Table 3. Semi-empirical (PM3) modelled energies of the silane-oligomers whilst the condensation-reaction of ATES

Step	Oligomer	H_2O	Energy PTES (au)	Energy iBTES (au)	Energy iOTES (au)
S1	monomer	26	-5.9295	-6.0053	-6.2549
S2	dimer	27	-5.9380	-6.0037	-6.2874
S3	trimer	28	-5.9486	-6.0084	-6.2992
S4	tetramer	29	-5.9577	-6.0221	-6.2973
S5	tetramer (1ring)	30	-5.9650	-6.0343	-6.3055
S6	pentamer	31	-5.9845	-6.0530	-6.3067
S7	hexamer	32	-5.9849	-6.0438	-6.3165
S8	*hexamer (2rings)*	33	-5.9863	-6.0577	-6.3145
S9	heptamer	34	-6.0067	-6.0680	-6.3300
S10	heptamer (3rings)	35	-6.0120	-6.0775	-6.3350
S11a	heptamer (4rings)	36	-6.0103	-6.0731	-6.3176
S11b	octamer	36	-5.9963	-6.0718	-6.3225
S12b	octamer (4rings)	37	-6.0124	-6.0874	-6.3532

For sets with PTES, the energy decreases from step S1 to S10, the main product. The energy of the sets for the next possible steps S11a and S11b, either intra- or intermolecular condensation, shows an increase. For sets with iBTES there is an increase in S2 and S7, for sets with iOTES there is an increase in S4 and S8. The energy of the steps S11a and S11b, the intra- or intermolecular condensation after the main product formation also increases for sets with iBTES and iOTES.

a) aaaa-isomer

b) aaab-isomer

c) aabb-isomer

d) abab-isomere
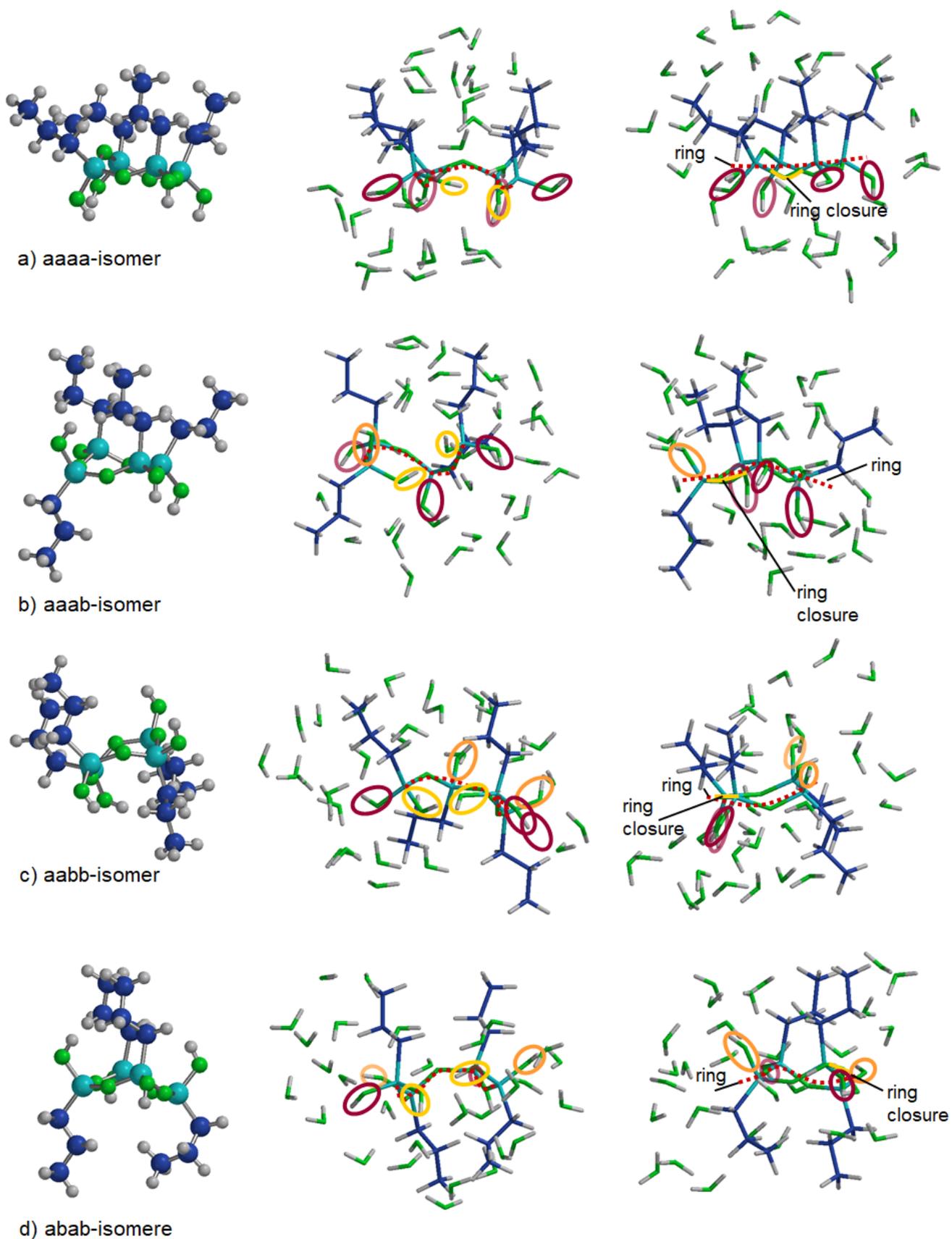
Fig. 5. The configuration of the four possible isomers for propyltriethoxysilane a) aaaa, b) aaab, c) aabb, and d) abab are shown in the first column. The second column shows the oligomer chains with additional water molecules immediately before the ring closure (step S4) and the third column shows the isomers with the additional water molecules after the ring closure (step S5)

3.4 Combination of experimental data and modelling results

Explanation for the forming of the T7O$_2$(OH)$_3$
From the MALDI/TOF-MS studies, the oligomer distribution for the three silanes shows the maximum for the T7O$_2$(OH)$_3$. Actually, this is an unusual oligomer featuring the geometry of a cube with one edge capped. One can typically expect oligomers with six or eight components. From basic geometrical considerations it can be deduced that the constitution of a T8 oligomer, a completely closed cube, requires an isomer with aaaa configuration in step S5.

The energies from the semi-empirical modelling of the sets in step S5 are the lowest for the aaaa isomer for PTES and for the abab isomer for iBTES and IOTES. The consideration of most of the alkyl groups corresponds to this result. The propyl group is the smallest; the branched alkyl groups are more voluminous and avoid approaching each other.

From the abab-isomer, the geometry with one edge capped cannot be achieved. Thus, the step S4 before the ring-closure is considered. It can be seen, that the sets in step S4 with the chain leading to the aaab-isomer have the lowest energies for all three silanes. A cube with one edge capped, can develop from this isomer. This step is therefore decisive for the geometry of the main product for the three ATES. For the three silanes the sets at step S11 and S12b with further inter- and intramolecular condensation show an increase of energy. This explains the stop of further assembly on this unusual oligomer.

Explanation for the differences in the oligomer distribution between PTES on the one hand and iBTES and iOTES on the other hand
If a possible route for assembling to a T7O$_2$(OH)$_3$ is investigated, PTES shows a decrease in the energy of the sets at each step. For the other two silanes, the sets of two steps are accompanied by an increase of energy. This suggests a slower constitution of the main product for iBTES and iOTES.

In addition, these steps indicate that a reverse reaction is possible for silanes with the branched alkyl group. The reverse reaction offers the possibility to mount another oligomer. The reaction of the PTES is faster. When the ring of the aaab isomer is closed and the next monomers are added, a ring opening back reaction becomes increasingly unlikely. The assembly of the propyl oligomer seems to be fast and kinetically driven, whereas for the iBTES and iOTES models it appears that the thermodynamically more favourable T8 oligomer can develop.

4.0 SUMMARY AND CONCLUDING REMARKS

Details of the reaction behaviour of organosilicon compounds in alkaline aqueous environments can be identified by a combination of computer chemistry and mass spectrometric investigations. In this way, the structure of the relevant siloxane oligomers was identified and various steps of their condensation in an alkaline environment were characterized. The understanding of such model systems provides the basis for a detailed understanding of the growth and structure of functional films formed on the surfaces of the mineral components within the pore structure of cement-based materials. This functionalization is closely linked to the alkyl groups of the chemicals used. In this context, the study also provides information on the role of different alkyl groups in the reactions. Furthermore, the modelling approaches developed here and the experimental concepts form the basis for a detailed investigation of the chemical degradation of the films. Therefore, new research activities have already been initiated to investigate the sturdiness of such measures in aggressive chemical environments and thereby to investigate the long-term effectiveness of the treatment of concrete with organosilicon compounds.

Generally, computational chemistry appears to be a powerful tool for the investigation of complex chemical reactions in the field of construction chemicals in general. By means of such methods, experimental data obtained for the reactions of silanes in the presence of mineral substrates can be qualitatively explained at the molecular level. Quantitative considerations are more difficult because the exact knowledge of the reaction mechanism of polycondensation is not completely available. However, with regard to a reliable investigation of processes as the polycondensation of the ATES in cement-based materials in the cement paste, a further difficulty arises. The atomic structure of CSH-gel as one of the essential constituents of cement paste cannot be described with exact atomic positions. Nonetheless, there are ways of overcoming this problem. For example, the structure of Tobermorite or Jennite, respectively, is often considered as a useful approximation (e.g. Churakov, 2009 and 2008, or Wang *et al.*, 2006). However, if the mineral material is not considered to be crystalline, but rather amorphous (Pellenq *et al.*, 2009), the modelling of such a solid surface is a great challenge in view of the required computing performance. However, promising strategies to get this under control reduce the consideration of solid surfaces as molecular clusters (e.g. in Feher *et al.*, 1989, and Dkhissi, 2004).

In particular, as computing performance and precision of the models improve rapidly, computational chemistry as a versatile instrument to support investigations in experimental, inaccessible systems and will therefore quickly gain importance. It is already a powerful tool for identifying essential factors related to the functionalization of mineral materials at the molecular level (e.g. Giraudo *et al.* 2018). Knowing these factors makes it possible to influence the reaction process by modifying the ATES. This is helpful when deciding on the use of additives and has the potential to significantly support the development of "tailor-made" construction chemicals.

Acknowledgement

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