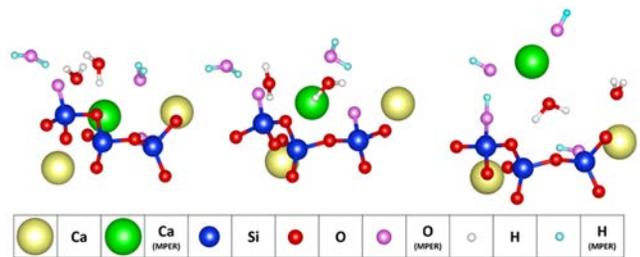


Exchange Reactions at Mineral Interfaces

Peter Thissen*

ABSTRACT: Exchange reactions are a family of chemical reactions that appear when mineral surfaces come into contact with protic solvents. Exchange reactions can also be understood as a unique interaction at mineral interfaces. Particularly significant interactions occurring at mineral surfaces are those with water and CO_2 . The rather complex process occurring when minerals such as calcium silicate hydrate (C–S–H) phases come into contact with aqueous environments is referred to as a metal–proton exchange reaction (MPER). This process leads to the leaching of calcium ions from the near surface region, the first step in the corrosion of cement bound materials. Among the various corrosion reactions of C–S–H phases, the MPER appears to be the most important one. A promising approach to bridging certain problems caused by MPER and carbonation is the passivation of C–S–H surfaces. Today, such passivation is reached, for instance, by the functionalization of C–S–H surfaces with water repelling organic films. Unfortunately, these organic films are weak against temperature and especially weak against abrasion. Exchange reactions at mineral interfaces allow the preparation of intrinsic, hydrophobic surfaces of C–S–H phases just at room temperature via a metal–metal exchange reaction.



INTRODUCTION

The interactions of mineral interfaces with water are of fundamental importance in nature. They play a significant role in the dissolution, deposition, and sorption processes of minerals as well as in the quality and composition of natural waters. They also affect soil formation, the uptake and release of plant nutrients, the volume of CO_2 in the atmosphere, the global cycles of the chemical elements, and the mobility of heavy metal impurities.^{1–3} They are also used to explain the sequestering of water on Mars and the formation of prebiotic molecules in the early history of the earth.^{4,5} Furthermore, the scientific understanding of the processes at mineral interfaces between aqueous solutions and solid surfaces is advantageous in the further development of catalysts, the corrosion and passivation of surfaces,^{6–11} the cleaning of semiconductor surfaces,¹² “chemical sensing,”^{13–17} and water treatment.

CO_2 is the gas mainly responsible for the greenhouse effect, so one of the human research community’s greatest efforts of the last century was regulating global warming by controlling its release into the atmosphere, even though it was only partially successful.¹⁸ Cement production releases a great deal of CO_2 . To reduce its release, many alternatives have been researched and are constantly in development. One such alternative is storing CO_2 by sequestering it through carbonation.^{19–22} It is well known that carbonates are present in many minerals, and their presence in C–S–H phases has been well characterized.^{23–25} C–S–H phases are quite promising (e.g., using

supercritical CO_2 conditions) if carbonates are considered to be desirable on the surface for a purpose such as CO_2 storage.^{26,27}

Because the impact of using hydrated cement for CO_2 storage on the concrete’s mechanical properties is unknown, such an application is a controversial topic. Today, cement bound materials are the most important building materials due to their advantages regarding the availability of raw materials, processing, usability, material properties, durability, and price.²⁸ However, the infrastructures are exposed to mechanical and chemical loadings, causing changes in the material itself. Consequently, these effects provoke technologically, ecologically, and economically expensive maintenance. A study published in 2014 reported that \$8.3 billion was spent in 2002 just to restore highway bridges and estimated that it would require an expenditure that was at least 1 order of magnitude higher to remove corrosion damage to all concrete based materials.²⁹ However, the molecular mechanisms of chemical and mechanical corrosion in cement bound materials are still not clearly understood.

One reason for the difficulty in generating new insights at the atomic level is the complex chemical performance of the relevant

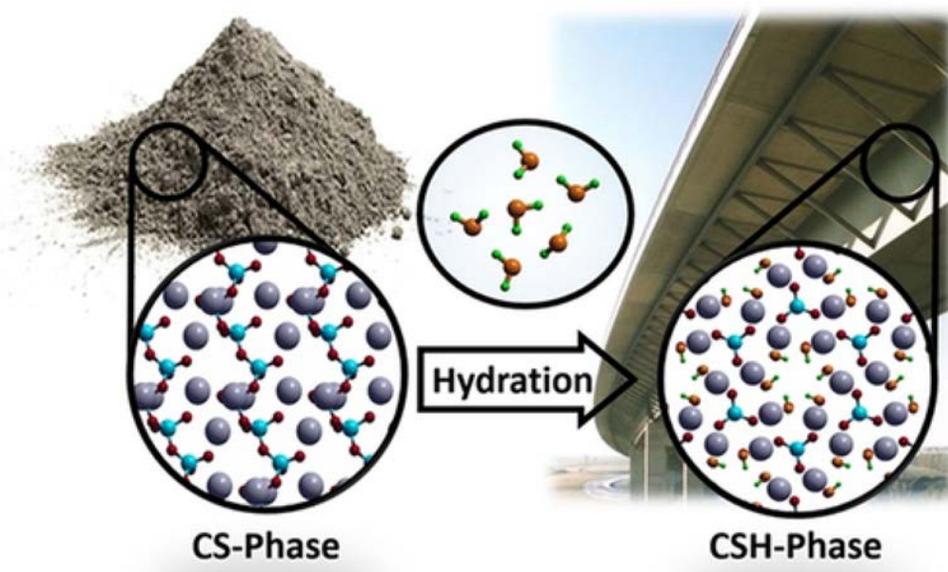


Figure 1. Binding material is formed by a series of chemical reactions that define the process of cement hydration. That is, the calcium silicates (C–S), in the presence of water, form hydration products that constitute a firm, hard mass made up mostly of calcium silicate hydrates (C–S–H). Reprinted with permission from *Chem. Eur. J.* **2018**, *24*, 8603. Copyright (2018) John Wiley & Sons.

mineral interfaces. Complex chemical performance in this context means that the structures are a mixture of both amorphous and crystalline phases, stoichiometries are not unique, and that the material is reactive for a very long time (years). Hydrated cement is composed mostly of C–S–H phases (Figure 1). The most important compounds of hydrated cement are the C–S–H phases, which primarily determine its mechanical properties.³⁰

These minerals have rather complicated structures, so it is difficult to reach a deeper understanding of their surface chemistry, even though the chemical processes that cause corrosion on such substrates are very important. Detailed atomic level information is rather scarce, as it is for many other minerals.³¹ Therefore, using the so called surface science approach would be desirable because of its success in understanding the surface chemistry of metals and, more recently, of some metal oxides.^{32–34} So far, there have been no reports that model reactions on well defined mineral substrates under ultrahigh vacuum (UHV) conditions have been investigated through spectroscopic methods. This is because there are experimental problems and the fact that infrared reflection–absorption spectroscopy (IRRAS) could not be used straightforwardly on bulk dielectrics’ surfaces.

Because detailed experimental information is lacking, it is impossible to validate theoretical examinations or to understand the details of even simple chemical processes on mineral surfaces, particularly on concrete surfaces. To study the water/solid interfaces of metal/water systems, a useful and supplemental tool is modeling that is based on *ab initio* density functional theory (DFT) (section 2.1). Atomistic modeling is of particular interest in this field of science because it can provide satisfactory microscopic descriptions of the investigated systems.

New insights into the surface chemistry of mineral interfaces are a prerequisite for the efficient and long lasting corrosion protection of structures made of cement containing building materials. The experimental and theoretical methods used so far are not sufficient to elucidate the molecular processes taking

place at these interfaces. Additionally, methods from surface chemistry have to be adapted and expanded for research related to construction chemistry. In this invited feature article, on the one hand, the results of experiments are presented and discussed, and on the other hand, atomistic first principles calculations are discussed. The use of model surfaces is the key to bridging the gap from applied to basic research.

Particularly important interactions occurring on mineral surfaces are the ones with water (section 2.3) and CO₂ (section 3.2). “MPER” refers to the complex reactions that occur when minerals containing C–S or C–S–H phases contact aqueous environments (section 3.1). In the case of C–S and C–S–H, the leaching of calcium atoms from the near surface region is a result of this process. Such leaching is the first step in the corrosion of cement bound materials (section 3).

SURFACE SCIENCE APPROACH

Generally speaking, the chemical behavior at the interfaces between cement bound materials and water raises many questions. The situation is quite different from that of metallic surfaces where the so called surface science approach (Nobel Prize, Gerhard Ertl, 2007) has gained a comprehensive understanding.³² In the case of oxide surfaces, there is much less acquired knowledge than in the case of metals, and knowledge has been initially achieved only for single crystal model substrates such as titanium dioxide and zinc oxide.^{34,35}

Very little is known about the surface chemistry of water containing hydrate phases of cement bound materials. An increase in knowledge pertaining to the chemical and physical behavior of the surfaces in cement bound materials and their components is thus of particular importance for improving the performance of these important materials. In order to apply the microscopic and spectroscopic methods of surface science, working with precisely defined model substrates is necessary.

Water Adsorption on Metal Surfaces. The interactions of water with solid surfaces play a central role in natural phenomena such as electrochemistry, rock efflorescence, corrosion, and catalysis and therefore has important applications

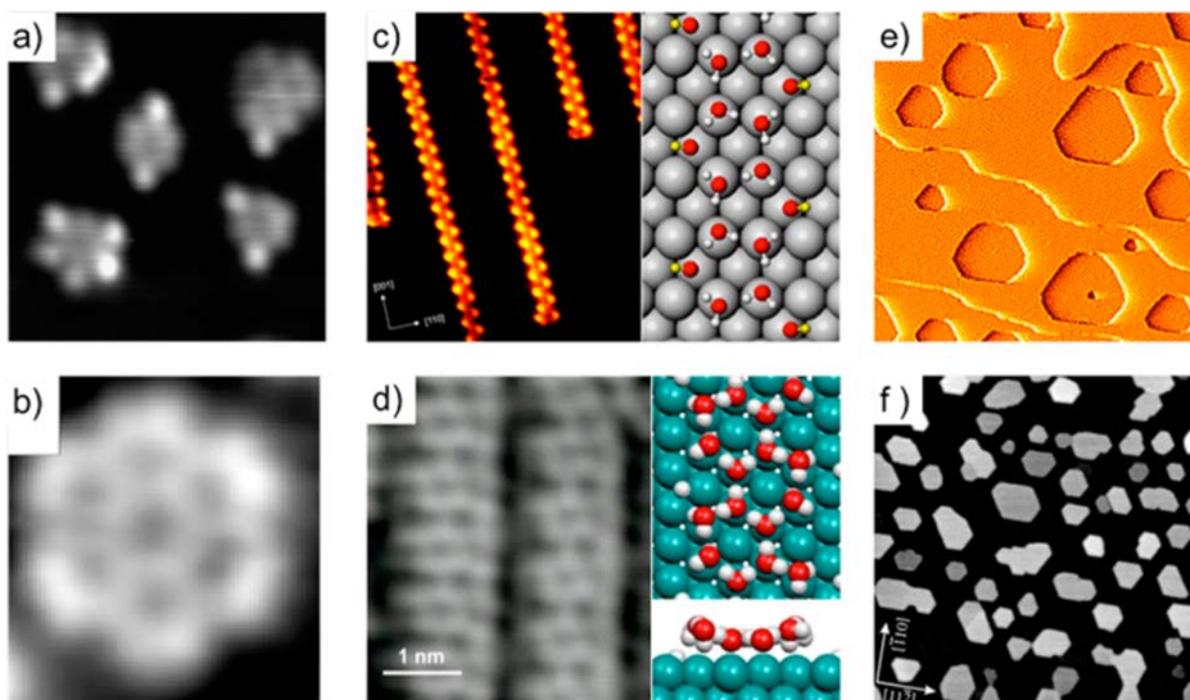


Figure 2. Different types of water structures formed at metal surfaces. One dimensional clusters on (a) Ru(0001) at 130 K⁴⁰ and (b) Pd(111) at 100 K.⁴¹ Two dimensional chains on (c) Cu(110) at 150 K⁴² and (d) Ru(0001) at 145 K.⁴³ Two dimensional layer on (e) Pt(111) at 140 K.⁴⁴ Three dimensional film growth on (f) Pt(111) at 140 K.⁴⁵ Reprinted with permission from *Chem. Rev.* 2016, 116, 7698–7726. Copyright (2016) American Chemical Society.

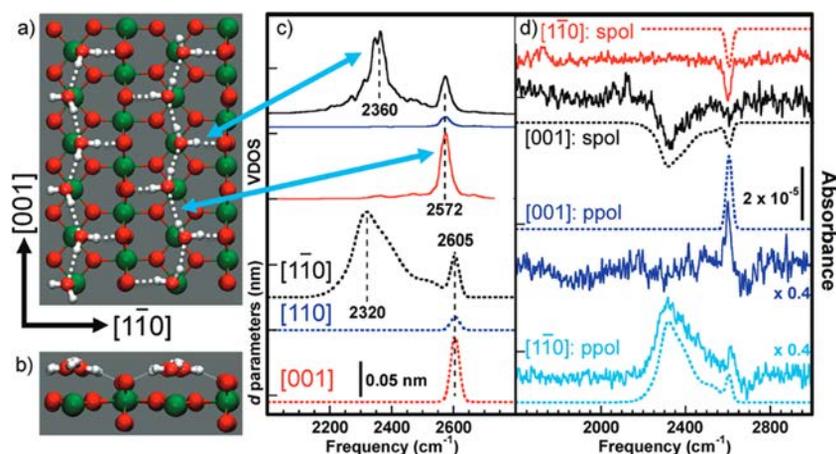


Figure 3. Structure of one monolayer of D₂O on TiO₂(110). (a) Top view and (b) side view of the calculated structure. (c) Calculated vibrational density of states (VDOS) versus frequency. (d) IRRAS spectra for s and p polarized light along both azimuths (solid lines) and simulated spectra (dashed lines). Reprinted with permission from ref 53. Copyright (2012) American Chemical Society.

in biological sensors, fuel cells, and hydrogen production.^{36,37} Over the last two decades, laboratories have used various experimental techniques for the intensive investigation of water adsorption on single crystalline metal surfaces. These techniques constitute a prototype system for understanding the interactions of water–solid interfaces.³⁸ Water forms various structures on metal surfaces, from isolated clusters and one dimensional chains to two dimensionally ordered multilayers, depending on the coverage and experimental conditions (Figure 2).³⁹

Earlier experiments used low energy electron diffractions (LEED) to study the ordered 2D structures, while the scanning tunneling microscope has been used in recent experiments to image and probe isolated water clusters locally.^{46,47} For example,

STM was used to observe water monomers, dimers, and hexamers on Ag(111), Cu(111), and Pd(111) surfaces.^{48–50} STM was also used to observe a 1D water chain on the steps of a Pt(111) surface.³⁹ Depending on the substrate, water forms hydrogen bonded networks of various phases as the coverage increases and grows into multilayers and bulk ice at high coverages. Feibelman suggested a half dissociated D₂O/Ru(0001) structure based on first principles calculations.³³ This model fits well to experimental findings from Held and Menzel based on LEED analysis.⁵¹ Today it is debated controversially if dissociation of water on metal surfaces is possible, and spectroscopic evidence is still missing.

Two fundamental forces that occur at the water–metal interfaces determine these adsorbed structures and their

stabilities: the water–surface interaction and the interwater hydrogen bonding. The former is found primarily in the water–metal contacting area, while the character and strength of the latter are modified by the presence of the substrates. These two interactions are comparable in strength on most metal surfaces. A rich class of adsorbed structures results from their competition, especially at submonolayer coverages. To understand the water–surface interaction, it is essential to characterize these structures at low coverages.

Water Adsorption on Oxide Surfaces. To understand many phenomena in atmospheric chemistry, corrosion, electronics, environmental protection, heterogeneous catalysis, and sensors, it is essential to understand the chemistry of water/solid interfaces.^{36,52} During ambient storage, the surface chemistry of most air formed oxide films on metals undergoes continuous changes.

Infrared (IR) spectroscopy is a powerful tool for investigating the chemical identity, structure, and dynamics of adsorbates on surfaces. Because the OH stretch frequency of H bonds depends on the chemical environment of the bond, IR spectroscopy is particularly useful for investigating H bonded systems, including thin water films. However, because the signals in Fourier transform infrared reflection–absorption spectroscopy (IRRAS) on dielectric substrates are typically an order of magnitude weaker than those on metals, relatively few experiments have been done on well characterized dielectric single crystals. Kimmel et al. have investigated the structure and dynamics of thin water films adsorbed on TiO₂(110) using IRRAS and ab initio molecular dynamics.⁵³ For a surface coverage of one monolayer, the D₂O adsorbs nearly parallel to the surface (Figure 3). Weak H bonds are formed between adjacent D₂O in the [001] direction, leading to a narrow, high frequency OD stretching peak (2572 cm⁻¹, Figure 3), while stronger bonds between D₂O and bridge bonded oxygen (BBO) lead to lower frequency OD stretching vibrations (2360 cm⁻¹, Figure 3) perpendicular to the BBO rows.

TiO₂ can easily be reduced, and the occurring defects mainly influence the water adsorption by the presence of one fold coordinated oxygen. Results from Diebold et al. provide evidence of complex behavior for adsorbed water, where dissociated and mixed dissociated–molecular adsorption states are thermodynamically favored at submonolayer and monolayer coverages, whereas the adsorption is purely molecular at greater coverages.³⁵ Equilibrium between dissociated and nondissociated species very often exists on many ionic substrates. For example, ordered structures with equal numbers of deprotonated and intact H₂O species have been reported for ZnO(10 10). For low surface coverages, the formation of pairs of dissociated and nondissociated water molecules has been investigated.^{54,55} In those cases, the hydrogen bonding between the partially dissociated water layer and surface hydroxyl groups yields a substantial stabilization of the structures.

Next, the focus will be on the elements which are strongly related to the formation of cement bound materials. For some time, the model for water interaction with metal oxide surfaces has been the well defined MgO(100) surface (e.g., hydroxide formation and carbonaceous pickup have been quantified at the oxide surface of magnesium).⁵⁶

It has been found that hydroxyl formation and carbonaceous adsorption have opposite effects on the ability of organic molecules to form chemical bonds with the oxide/hydroxide surface. Before the controlled adsorption of organic molecules to this surface can be investigated, the oxide surface of magnesium

stored under ambient conditions must be characterized in detail. The macroscopic corrosion of magnesium has been looked at in a number of studies, but very few of them investigated the chemical changes of the oxide surface due to atmospheric exposure. When exposed to ambient conditions, a visible film will form on clean, unprotected, standard purity magnesium surfaces.⁵⁷ It is believed that, in general, atmospheric attack under damp conditions results in the formation of a superficial MgO layer on the pure magnesium metal. Nordlien performed an experiment in which magnesium was scratched after being exposed to the ambient atmosphere for 60 min. Transmission electron microscopy (TEM) and electron diffraction verified that, after being scratched, a film described as a dense mixture of crystalline Mg(OH)₂ and amorphous MgO formed on the magnesium.⁵⁸ In addition, water adsorption on the MgO(100) surface has been studied computationally. Giordano et al., Odelius, and Delle Site et al. performed first principles calculations that predicted water dissociation on the atomically flat MgO(100) surface.^{59–61} On the other hand, the acidic dissolution of the MgO(100) surface was addressed by semiempirical quantum chemistry calculations.⁶² Changes in the topography of the MgO(100) surface during dissolution were reported in studies using atomic force microscopy (AFM). In dilute acid (pH 1 to 2) and water, rectangular/square pits were reported for the MgO(100) surface.^{63,64} The pits appeared as partially asymmetric inverted pyramids. They contained edges several micrometers long, took many minutes to form, and reflected an advanced stage of dissolution. The erosion of steps and edges caused by MgO's exposure to high humidity was reported in other AFM studies. However, the formation of etched pits was not reported by those studies.^{65,66}

Concerning pH dependent stability, the parameter free prediction has strongly developed on the basis of work carried out within density functional theory. In a study published in 2012, an etching mechanism for MgO(100) single crystal surfaces using density functional theory has been proposed and later been confirmed experimentally by an in situ scanning force microscopy measurement.⁶⁷ The following year, these results were used to decipher the toxicity of MgO nanoparticles toward cancer cells.⁶⁸

The interaction of water with aluminum oxide surfaces has attracted interest due to the broad use of this material as a catalyst, as a catalyst support, and in environmental chemistry. Furthermore, a widely studied model for the interaction of water with metal oxide surfaces is the well defined Al terminated Al₂O₃(0001) surface. Most experimental studies propose water dissociation on the Al terminated Al₂O₃(0001) surface. This was concluded from high resolution electron energy loss spectroscopy as well as from thermal desorption experiments (TDS).^{69–71}

Amorphous SiO₂ is very important because it is widely prevalent in natural minerals and commonly used in semiconductor technology (section 2.3). A mixture of the (111) and (100) surfaces of hydroxylated β cristobalite, which expose single and geminal hydroxyl groups, respectively, usually models the surface of amorphous SiO₂. These groups are close enough to each other on a fully hydroxylated (100) surface to allow H bonded networks to form. The hydroxyl groups are more widely separated on the (111) surface, so no H bonds can form between them.⁷²

Both theoretical and experimental studies have been conducted on the structure of water on various SiO₂ surfaces.^{73–81} An ordered hexagonal water layer on the

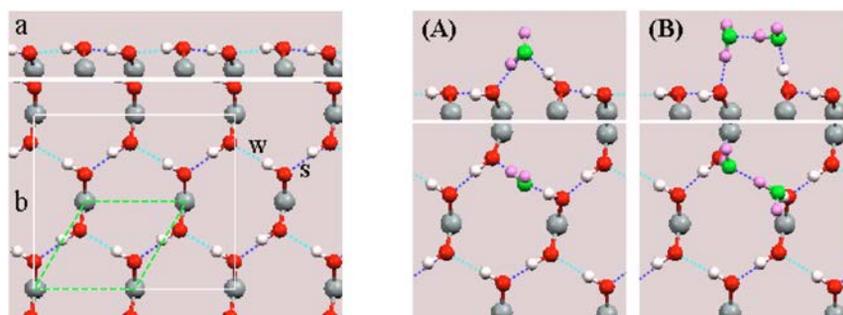


Figure 4. (Left) Optimized geometry for the clean hydroxylated quartz(0001) surface: (a) side view and (b) top view. For clarity, only the surface atoms are depicted here: large gray spheres for silicon, medium sized black spheres for oxygen, and small white spheres for hydrogen. The strong and weak surface H bonds are depicted with dark and light gray dotted lines and marked as S and W, respectively. The gray dashed lines show the hexagonal surface unit cell, while the white lines depict the tetragonal surface cell used in the present work. (Right) Optimized geometries for adsorbed monomers A and dimers B depicted from both the side and top views. The oxygen O_w and hydrogen H_w in the adsorbed H₂O are colored differently from those on the surface: medium sized gray green for O_w and small light gray violet for H_w. Reprinted with permission from *Phys. Rev. B* **2006**, 73, 035406. Copyright (2006) American Physical Society.

hydroxylated surface of quartz(0001) (Figure 4) and a hexagonal ice like structure on a fully hydroxylated β cristobalite(100) surface were predicted by these studies, but controversy has arisen about whether such monolayer structures are stable at room temperature. There has been no prediction of an ice like structure for water on cristobalite(111). A hollow site with molecules forming two or three H bonds with surface silanol groups has been predicted as being most favorable for water molecules. Optical experiments suggest that an ice like monolayer would form on amorphous SiO₂ at room temperature and 10% relative humidity. Information is much scarcer about the structure of water films that are thicker than a monolayer. A mixture of ice like and water like structures has been shown on the surface of quartz(0001) immersed in water by sum frequency vibrational spectroscopy experiments. The growth of water on amorphous SiO₂ has been studied through infrared experiments. Researchers have suggested an ice like growth of the water film of up to three to four monolayers, followed by a liquid water film above that, by assigning various features of the spectra to ice like and liquid like water.

Water Adsorption on Mineral Surfaces. The research on mineral/water interfaces is significantly less advanced than the research on metal or metal oxide/water interfaces. The difficulty of producing defined substrate surfaces is the main reason for this. One approach to close this gap is the development of reproducible model substances, as revisited in this invited feature article. The use of model surfaces is the key to bridging the gap between applied and fundamental research.

In early studies, tobermorite and jennite were employed as C–S–H models.^{95–97} Pellenq et al. proposed the so called realistic model of cement hydrate in 2009. Since then, this model has been updated via implementation of the reactive force field method, yielding results close to the experimental findings.⁹⁸ This model has been extensively employed to study the structure, dynamics, and mechanical properties of cement at the nanoscale. Considering the high computational demand of quantum mechanical simulations, Longo et al. used CaSiO₃ to simulate C–S–H models rather than tobermorite, jennite, or the realistic model.⁹⁹ The simulation of the structure of CaSiO₃ is less computationally demanding. It should be mentioned that there are discrepancies between CaSiO₃ and the real cement hydrate. However, even more significant discrepancies exist between the bulk and surface slab cells used for these simulations, making a meaningful comparison difficult. In

Table 1. Recent Studies on Mineral Model Systems

| system | applied technique | state | ref |
|----------------------------------|-----------------------------|------------------|--------|
| minerals | perspective | 2001, 2014 | 1, 82 |
| SiO ₂ | DFT | 2005 | 83 |
| CaCO ₃ | IR, DFT, AFM | 2013, 2020 | 84, 85 |
| CaSO ₄ | SEM, XRD | 2019, 2020 | 86 |
| CaSiO ₃ | IR, DFT, AFM, Titration | 2004, 2009, 2014 | 87, 88 |
| Tobermorite 11 Å | titration, Monte Carlo, DFT | 2014 | 89 |
| Ca ₂ SiO ₄ | DFT, force field | 2012, 2014, 2015 | 90 93 |
| Ca ₃ SiO ₅ | DFT, force field | 2012, 2014, 2015 | 90 93 |
| MgSiO ₃ | titration | 2009 | 88 |
| Al ₂ O ₃ | DFT, AFM | 2009 | 94 |
| MgO | DFT, AFM | 2012 | 67 |

most of the previous studies, only models of the bulk material have been considered, whereas in future work a computational examination of surfaces and surface/water interfaces will be necessary. Furthermore, the previous literature bulk models excluded CO₂ and the resulting reactions.

A form of calcium silicate (CaSiO₃), in which Si–O tetrahedral groups form a chain like structure running along the [010] direction of the bulk composition, is called wollastonite. Two apex joining Si–O tetrahedra combine with one Si–O tetrahedron in which one edge is oriented parallel to the chain direction. The coordination of calcium ions connects these Si–O chains to each other. In the presence of water, which already exists in alkaline media because of the MPER, the mineral surface stoichiometry changes. Consequently, the wollastonite(001) mineral/water interface is enriched, relative to the composition of the bulk material, in Si–OH sites.

Zeolites have been similarly studied.^{100–102} Zeolites are among the most important materials in heterogeneous catalysis. They are silicates in which aluminum replaces the calcium that is present in wollastonite. IR spectroscopy in transmission mode has been extensively used for the study of zeolite powders. The identification of adsorbate vibrations in these compounds is severely hampered by the excitation of substrate phonons. Van Santen et al. used careful, sophisticated analysis to demonstrate that protonating Brønsted sites, which are bridging hydroxyl

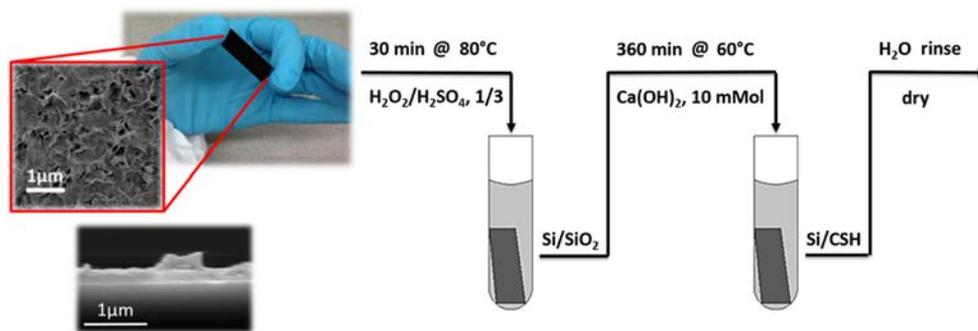


Figure 5. (Left) Ultrathin calcium silicate hydrate (C–S–H) phase grown on a silicon wafer. Under the electron microscope, the rough surface and the porous structure of the C–S–H phase can be observed. After a cross section, a representative image of the C–S–H phase under the electron microscope is possible to estimate the layer thickness (in this case, about 300 nm). (Right) Possible synthesis for growing C–S–H phases on a silicon wafer.

groups, causes a shift in T–O lattice mode frequencies (with T representing combined silicon and aluminum sites).

Experimental evidence shows that if water is close to solid interfaces then its dielectric constant is an order of magnitude smaller than the dielectric constant of bulk water at room temperature. On mica, for example, it is ~ 4 at the interface compared to ~ 78 in bulk water.¹⁰³ These are indications of (A) the ability of water molecules to orient themselves relative to the surface and of (B) the change in chemical reaction conditions at interfaces. It has been known for a long time that the structure and physical properties of the water close to mineral surfaces differ significantly from those of bulk water. These differences could be key to understanding the chemical processes at mineral interfaces with aqueous solutions in the future. However, the dielectric constant is a macroscopic property and does not provide a satisfactory microscopic description.

Formation of Ultrathin Calcium Silicate Layers on Silicon. Recently, it was demonstrated that it is possible to grow ultrathin (i.e., nanometer thick) C–S–H and C–S phases on single crystal silicon wafers (Figure 5).¹⁰⁴ This method is advantageous in the context of investigating natural C–S–H and C–S phases. The synthetic phases can be produced in a glovebox with very high purity and with ideal reproducibility. In addition, the synthesis can be flexibly altered to take account of important aspects of the phases (e.g., the Ca/Si ratio of the product) or the layer thickness. The ultrathin C–S–H and C–S phases produced are ideally suited for research and industry.^{99,104–106}

The model surfaces allow the use of new and meaningful experimental and theoretical methods, which have previously been only conditionally applicable to macroscopic mineral surface samples.⁸⁷ Also, the synthetic ultrathin C–S–H and C–S phases have led to further interesting applications.

Because of their unique chemistry, several interface applications can be developed on the basis of the C–S–H and C–S phases on silicon wafers. These substrates are promising materials for use as sensors for phosphates in wastewater⁹⁰ and even for other elements that have to be either recovered or urgently removed to avoid serious health problems, such as arsenates.¹⁰⁷ Furthermore, the direct surface synthesis of essential compounds such as calcium phosphates, for example, hydroxyapatite, which are significant for medicinal use due to their compatibility with bones and bonelike structures, can be achieved. Also, using these substrates for doping silicon wafers with phosphorus seems to be very feasible for the manufacture of semiconductors.¹⁰⁸ The exchange of calcium by other metals

(e.g., nickel) can be easily performed, providing an interesting foundation for research in heterogenic catalysis. As a result, successfully developing those applications is primarily dependent on the accuracy and reproducibility of the production of these presented substrates. The relevant synthesis factors depend on the final application.

EXCHANGE REACTIONS AT CEMENT-BOUND MATERIALS

Concrete is one of the most complex substances known to materials science, and it is also our most important construction material. Because it is very porous, we urgently need to better understand its surface chemistry, especially its reaction with water, to avoid the corrosion of buildings, bridges, and other infrastructure. The surface science approach to studying wollastonite, which is a well defined mineral, gave insight into the proton transfer within concrete when it contacts water. The fact that dissociation and the formation of OH species result from the exposure of this C–S substrate to H₂O was revealed by data from IR spectroscopy. Because it triggers the hydration of cement on the one hand while governing the corrosion of concrete on the other hand, this proton transfer is a very important reaction. It is interesting that when the same surface is exposed to methanol there is no proton transfer.

Metal–Proton Exchange Reaction. The leaching of metal ions, especially calcium, out of concrete is caused by the MPER, resulting in massive structural changes in the corresponding C–S and C–S–H phases. Most of the details and implications of this reaction are not well enough understood, even though it has been studied extensively. To study the MPER's important aspects, the mineral wollastonite was used as a model system in 2016. The most important role of this study was demonstrating that, in aqueous environments, a crucial consequence leads to shape changes of the micrometer sized particles.¹⁰⁹ Oelkers et al. investigated the MPER on different minerals and concluded that the number of protons consumed by this exchange reaction is mineral specific.¹¹⁰ Recently, Giraudo et al. were able to derive a more comprehensive theoretical description and identified the pH of the aqueous environment as a parameter of key importance.¹¹¹

They measured different silicon and calcium concentrations at varying pH of the solution through experimentation. Their results are shown in Figure 6A, where the blue line corresponds to the blue X axis and the red lines correspond to the red Y axis. The Y axes have the same scale, so they can be directly compared. The concentrations in wollastonite measured at varying pH levels are represented by the blue points. As a reference system, the silicon concentration in wollastonite is represented by the red diamonds. At every pH level in the aqueous medium, the calcium concentration is higher than the concentration of silicon with respect to the MPER. The concentration of silicon is represented by the red square points; it was measured in the aqueous medium with SiO₂ as a reference system. Both materials are most stable in the neutral regime of pH, so there is unquestionably a clear

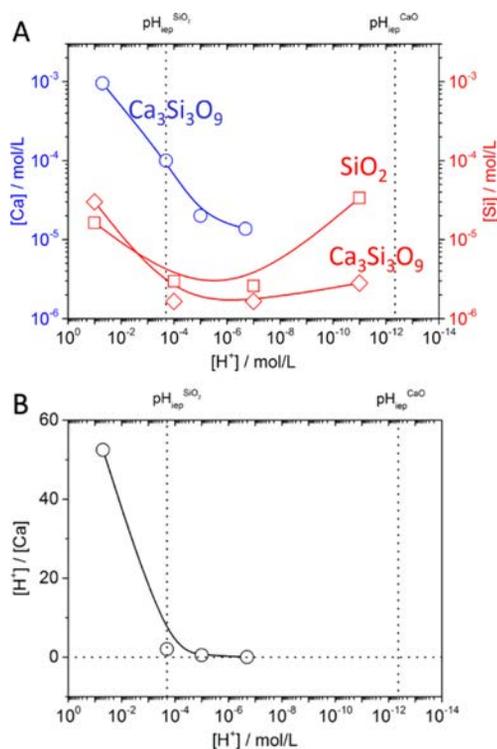


Figure 6. (A) Inductive coupled plasma atomic emission spectroscopy was used to measure the concentration of silicon and calcium as a function of the concentration of protons, as shown here. (B) Number of protons consumed by the preferential exchanged calcium as a function of the concentration of protons ($\text{pH} = -\log[\text{H}^+]$) applied at the water/wollastonite interface. Reprinted with permission from *J. Phys. Chem. C* **2015**, *119*, 10493–10499. Copyright (2015) American Chemical Society.

relationship between them. As reported by Brinker, the classic hydrolysis curve of silicates is observed in SiO_2 .¹¹² It was found that wollastonite is just as stable in very alkaline media as in neutral pH, even though SiO_2 is known to be etched in such media. This is because the calcium ions between the silicate chains have very strong cohesion.¹¹³ The relationship between calcium ion exchange and proton concentration can be represented with the same data. Figure 6B shows that ratio. At different pH levels, calcium in wollastonite is diversely exchanged. In the basic and neutral regimes ($\text{pH} 14\text{--}4$), there is good agreement with the predicted values; in the acidic range ($\text{pH} < 4$), an increasing mismatch appears, which can be explained by the fact that nonequilibrium etching dominates the MPER.

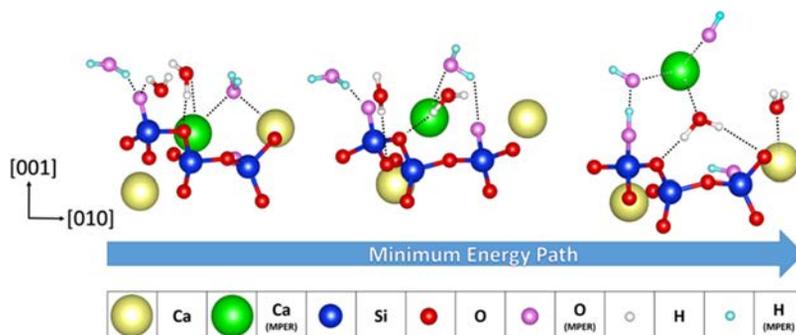


Figure 7. Metal–proton exchange reaction (MPER) at the wollastonite(001)/water interface. One possible mechanism is described in this figure. In the initial state (left side), a dense network of molecular water has formed on the surface. Next, calcium is lifted from its initial position (transition state, middle of the figure). In the final state (right side), water dissociates, two protons penetrate to the wollastonite surface, and $\text{Ca}(\text{OH})_2$ forms. Adapted from *J. Phys. Chem. C* **2016**, *120*, 22455–22459. Copyright (2016) American Chemical Society.

The structural failure of concrete based buildings has many possible causes: rapid heating–cooling cycles resulting from day/night temperature changes, mechanical stress caused by vehicles, and the corrosion of supporting (metal) bars, among others. But the interaction of water with the C–S and C–S–H phases that form the structural base of concrete is one of the biggest problems.

MPER induces the corrosion of cement bound materials, causing a phase transformation of crystalline to glassy C–S–H phases. Protons from the water replace calcium in the structure (Figure 7) because of the MPER on the wollastonite. As a result, the shape of the crystals is modified, leading to their amorphization. If the surface orientation is perpendicular to the silicate chain direction, then the MPER has higher reaction rates.

The mechanical properties of these compounds, such as hardness and stiffness, are greatly dependent on the length of the silicate tetrahedral chain, which also determines how the MPER will affect their structure. Hou et al. have shown that the silicate chain length depends on the Ca/Si ratio.¹¹⁴ Wollastonite has infinitely long chains and a Ca/Si ratio of 1. No long chains are present before heating in C–S–H phases that are synthesized in aqueous solutions and no long chains are present before heating, so it is hypothesized that the resulting chain length after heating decreases with increasing Ca/Si ratio. The notion that the temperature of dehydroxylation has to decrease for increasing Ca/Si ratios stems from the hypothesis that the chain is lengthened by the increment of the Ca/Si ratios.

The MPER, which is schematically represented in Figure 7, is the most important of the various corrosion reactions of C–S and C–S–H phases.

Carbonation Competing Surface Functionalization of Cement-Bound Materials. The earth's atmosphere contained $\sim 0.04\%$ CO_2 and $\sim 4\%$ H_2O in 2016,¹¹⁵ which is a major reason for the ubiquity of carbonate layers on cement and concrete. There is a lack of available knowledge about the carbonation reaction mechanism, even though that reaction is one of the most important processes in construction chemistry,

In the literature concerning the theoretical analysis of cement carbonation, there often is a significant discrepancy between the used models and the actual chemical composition of cement. $\text{Ca}(\text{OH})_2$ is usually taken as a model of the cement phase. Montes Hernandez et al. used infrared spectroscopy to investigate the kinetics of carbonation of solid $\text{Ca}(\text{OH})_2$ in 2010 and found an activation by molecular water that was adsorbed on the solid.¹¹⁶ Funk et al. quantified this water activation in a 2013 density functional theory (DFT) study.¹¹⁷ The difference between a water assisted and a water free reaction pathway was explained with the help of first principles calculations. The importance of amorphous carbonate being kinetically favorable over crystalline phases was emphasized by Black et al. as early as 2007.¹¹⁸

Longo et al. described the MPER on wollastonite besides CO_2 to understand the dependence of carbonate formation on the presence of water (Figure 8).⁹⁹ One of the most important conclusions of their

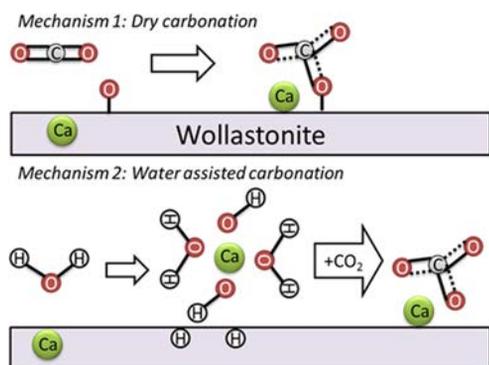


Figure 8. Mechanism 1, dry carbonation: Very fast carbonate production results from the exposure of CaSiO_3 to CO_2 . As shown in Figure 7, the surface of wollastonite contains unsatisfied oxygen atoms (purple oxygen in Figure 7). The CO_2 forms CO_3 complexes when it reacts with the surface oxygen. The reaction stops as soon as a carbonate monolayer has been formed. Mechanism 2, water assisted carbonation: The chemical potential of water in the environment strongly influences the reaction. A completely different mechanism is followed by the adsorption of CO_2 on CaSiO_3 with a water monolayer. In the first step, calcium is removed from the surface by the metal–proton exchange reaction. MPER can be considered to be a realistic scenario for describing the reaction with CO_2 because the thermodynamic ground state of calcium silicate phases in equilibrium with water is reached fast enough. In a second step, calcium hydroxide is now available for the CO_2 in the solution. Reprinted with permission from *ACS Appl. Mater. Interfaces* **2015**, *7*, 4706–4712. Copyright (2015) American Chemical Society.

work is that the carbonation reaction on wollastonite where MPER has succeeded forms calcium carbonates very quickly due to the high availability of calcium on the surface. On surfaces where MPER did not take place, CO_2 will still adsorb but bind weakly and thus form only a monolayer of carbonate. The reaction product is predicted to be CaCO_3 if the calcium was fully mobilized by MPER and $\text{CaSiO}_3\text{CO}_2$ if not fully mobilized; corresponding structures have been calculated and are presented in the literature.^{87,118}

The passivation of C–S–H surfaces is one approach to bridging the problems caused by MPER and carbonation. Functionalizing such surfaces with water repelling films of polysiloxanes (silicones) is one possible method of passivation. Molecules such as tetraethyl orthosilicate (TEOS) can bind with hydrated cement.

However, because the nature of such binding is unknown, it is not clear how C–S–H surfaces would interact with polysiloxanes. In addition, C–S–H phases are more difficult to passivate because of their lower reactivity toward siloxanes, which is due to the fact that they are normally carbonate terminated. As observed by Okhrimenko et al., upon the adsorption of alcohols on calcium carbonate, the alcohol tends to be oriented such that the hydroxyl oxygen is positioned toward the calcium ion while the hydroxyl hydrogen is positioned toward the carbonate oxygen, thus effectively buffering the local ionic charges of both surface ions.⁸⁴ As no dissociation is observed, no molecule binds tightly to the carbonate surface. We draw the conclusion that the carbonates should be removed (surface activation)¹⁰⁵ because they cannot bind strongly with functionalizing molecules.

Possible Restoration of Cement-Bound Materials by Alcohol Compounds. The proton exchange between adsorbed molecular species and the mineral surface, which leads to the formation of surface OH species, is the obvious first step in the MPER. This process has been studied on well defined surfaces of a macroscopic, crystalline C–S phase, wollastonite, by using CH_3OH as a probe molecule. The interlayer space containing interstitial water is exhibited in most other models and C S H phases leading to a strong reconstruction of these materials under UHV conditions. It is an important advantage of wollastonite that the occurring interlayer spaces are so small that no interstitial water is present.

In Figure 9 the black line depicts IRRAS measurements recorded for the clean wollastonite substrate exposed to H_2O vapor at room

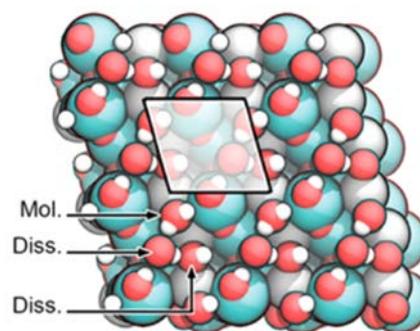
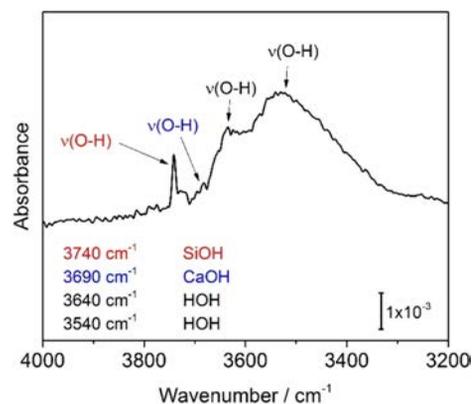


Figure 9. Infrared spectrum of H_2O adsorbed on wollastonite at room temperature, referenced to the clean wollastonite surface. Structure of an energetically favorable water monolayer adsorbed on wollastonite(001). Reprinted with permission from *J. Phys. Chem. C* **2014**, *118*, 8007–8013. Copyright (2014) American Chemical Society.

temperature. Indeed, the adsorption of water leads to the coexistence of Si–OH (3740 cm^{-1}) and Ca–OH (3690 cm^{-1}) groups on the wollastonite surface. The calculated Si–OH, Ca–OH, SiO–H, and CaO–H bond lengths amount to 1.64, 2.21, 0.96, and 0.97 Å, respectively. The Ca–OH groups are placed in the bridge position between two Ca atoms. Both the Ca adsorbed and the Si adsorbed OH groups are tilted by 33° with respect to the surface normal. These findings are in good agreement with recent findings reported by Sanna et al.⁸⁷

The presence of intact methanol on the surface is also strongly supported by the IR data reproduced in Figure 10, recorded after exposure to nondeuterated methanol (CH_3OH). The band observed for s polarized light at 1360 cm^{-1} is identified as the C–O–H deformation mode. A weak but significant interaction of the methanol OH group with the substrate is indicated by a substantial red shift (14 cm^{-1}) with respect to the gas phase (1346 cm^{-1}) that appears in this band. In addition, two weak features that are observed for s polarization at 1177 and 1157 cm^{-1} can be related to the characteristic splitting of the CH_3 umbrella mode in intact, fully protonated methanol. These assignments are in full agreement with the results obtained after exposure to perdeuterated methanol. The expected isotope shifts are shown in all vibrational modes.

Furthermore, evidence for a strong orientation of the methanol C–O–H plane along the *b* axis of the substrate is given by the appearance of the C–O–H deformation mode in s polarization at 1360 cm^{-1} but not in p polarization.

Figure 10 depicts the geometry of adsorbed methanol. The orientation of the adsorbed, intact methanol species fully agrees with the results of the IR data recorded for different polarizations (Figure 10). Molecular methanol is bound via the O atom to substrate Ca (Ca–O distance 2.32 \AA). The formation of a hydrogen bond to a substrate O

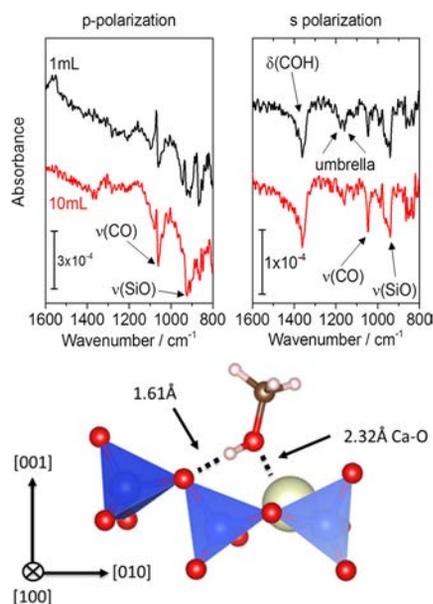


Figure 10. Infrared spectra of 1 mL of CH₃OH on wollastonite adsorbed at 100 K (black line) and 10 mL of CH₃OH on wollastonite adsorbed at 100 K (red line). Spectra are referenced to clean wollastonite. Reprinted with permission from *Chem.—Eur. J.* **2018**, *24*, 8603. Copyright (2018) John Wiley & Sons. Energetically favorable adsorption structure of methanol on wollastonite(001). The experimental findings reported above are in full agreement with the results of our theoretical analysis, which yields a binding energy of 1.2 eV for single methanol species adsorbed on the wollastonite(001) surface. A hypothetical dissociated species is found to be less favorable in energy by 0.5 eV.

atom with the (Si–O)–H distance amounting to 1.61 Å adds energy. The appearance of the C–O–H deformation mode in s polarization at 1360 cm⁻¹ but not in p polarization is nicely explained by this adsorption geometry, with a Ca–O–H angle of 84.4° and a Ca–O–C angle of 136.6°.

In order to investigate the sensitivity of methanol to the particular wollastonite orientation, we have also conducted a theoretical analysis of methanol bound to the wollastonite(100) surface. The atomic arrangement on this surface is quite different compared to that on the (001) surface. Equivalently, on this surface the intact methanol species is more stable than the dissociated one, but the binding geometry is, as a result of the different surface structure, quite different. The computed IR vibrational bands are clearly different: (1) The calculated frequency of the (COH) vibrations is considerably higher (1424 cm⁻¹) than the frequency computed for the (001) surface (1380 cm⁻¹) and the frequency seen in the experiment (1360 cm⁻¹). (2) The splitting of the CH₃ umbrella mode amounts to only 3 cm⁻¹, compared to 21 cm⁻¹ for the (001) substrate. We feel that we can rule out the presence of a substantial fraction of the substrate exposing surfaces other than (001) because the experimental splitting amounts to 20 cm⁻¹. The main reasons for these shifts in the vibration modes can be understood on the basis of the structural configuration of methanol adsorbed on a wollastonite(100) surface in contrast to the wollastonite(001) surface. The dihedral angle of H–C–O–H is nearly zero in wollastonite(001). As a result, the umbrella mode dissipates part of its energy to the OH. Because of high dihedral angles, this phenomenon was not found in other surface orientations.

Finally, we want to focus on the adsorbate induced relaxation of the wollastonite(001) substrate atoms, as derived from calculations. Even for the fairly strong Si–O bond, a slight contraction, by 0.1 Å, is observed upon methanol adsorption. Interestingly, methanol adsorption does not change the Si–O tetrahedron's volume. After hydrogen bond formation, the unsaturated Si–O bond (p polarization at 1069 cm⁻¹) shortens, but the volume of the tetrahedron remains constant

because the other three Si–O bonds (p polarization at 945 cm⁻¹, s polarization at 940 cm⁻¹) elongate.

The interaction of methanol and water, respectively, with this model mineral is quite different (Figure 11). The latter quickly dissociates on C–S and C–S–H surfaces, the first step in the MPER process.

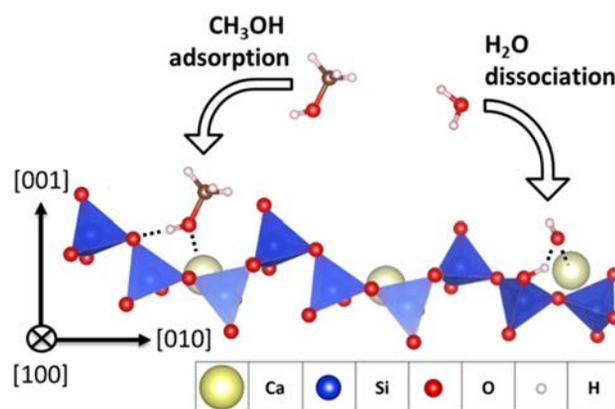


Figure 11. Molecular adsorption of methanol on the wollastonite(001) surface in contrast to proton exchange during the water adsorption on the surface. The finding of this obviously different chemical interaction is an important point for the future to develop new chemical products acting on the surface of minerals.

The different findings for methanol suggest the application of alcohol based calcium (calcium alkoxide) suspensions. Very recent results show that Ca(OH)₂ particles react with ethanol and isopropanol and partially transform into Ca ethoxide and Ca isopropoxide, respectively.¹¹⁹

New Hope for the Future: Metal–Metal Exchange Reaction.

The most promising of all techniques so far was the passivation of cement bound materials by phosphonic acids; corrosion slowed down because this method caused surfaces to repel water (Figure 12).¹²⁰ Passivation is possible without further previous activation and under the right conditions because these molecules are also able to react in the presence of carbonates.

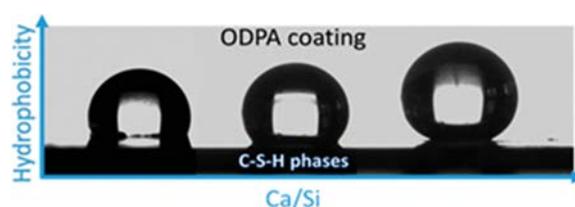


Figure 12. Water contact angle measurements of C–S–H phases coated with octadecylphosphonic acid (ODPA). (Left to right) Three C–S–H phases with different Ca/Si ratios. Reprinted with permission from *ACS Sustainable Chem. Eng.* **2018**, *6*, 727–737. Copyright (2018) American Chemical Society.

The results were very promising when this method was applied to a piece of hydrated cement because the amount of leaching calcium was significantly less at the passivated samples.

Today, using water repelling organic films to functionalize the C–S–H surface is a method of reaching such passivation. Unfortunately, these organic films are weak against temperature and especially weak against abrasion. Adapting the MPER to a new synthetic process for minerals, called metal–metal exchange reaction (MMER), Burek et al. were able to prepare an intrinsic hydrophobic surface of C–S–H phases at room temperature. Such a material extends the service lifetime of cement based materials because it is robust in a harsh environment. After being grown on silicon wafers, C–S–H phases were brought into contact with a Eu(III) solution at room temperature to achieve this inorganic

hydrophobization.¹²¹ The surface properties of the C–S–H material undergo several changes because of the exchange of the ions, and the properties of rare earth metal oxides can be changed immensely by doping.

A totally new platform that improves the resistance of cement and concrete surfaces against corrosion is created, depending on the type of metal exchanged. The presented approach controls the adsorption of fluids into the pore structure through an intrinsic and inorganic modification of the C–S–H compounds. The hypothesis is that the interactions of cement bound materials with aqueous solutions are determined by the structure and composition; therefore, the incorporation of ions other than calcium in C–S–H phases has a significant impact on their surface chemistry. The feasibility of using pure, ultrathin C–S–H layers has been demonstrated in this invited feature article. How the hydrophobicity of ceramic surfaces can be changed by doping those ceramics with rare earth metals was explained by Azimi et al. in 2013.¹²² When they are doped with oxides, these elements have an octet outer shell that prohibits any interaction with water molecules at the interface. Temperature has not driven the presented doping of rare earth oxides into the C–S–H phases, which would destroy the samples and would not be applicable to commercial cement later on. However, the sorption of Eu(III) in C–S–H results from a combination of diffusion and capillary transport. The exchange of Ca(II) for Eu(III) is underlined by detailed spectroscopic results (Figure 13).

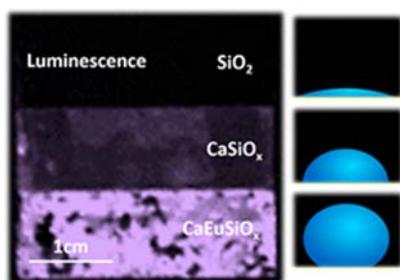


Figure 13. (Left) Luminescence of clean SiO₂ (top), synthesized C–S–H (middle), and C–S–H with 0.2 atom % exchanged Ca(II) vs Eu(III) (bottom). (Right) Water contact angle on the corresponding surfaces (compare with the picture on the left). Reprinted with permission from *ACS Sustainable Chem. Eng.* **2018**, *6*, 14669–14678. Copyright (2018) American Chemical Society.

New perspectives are opened up by this approach. One such approach is to address the transport properties of the rim zone of cement bound materials, which is indispensable for chemical resilience in hostile environments.¹²³ Moreover, there is an appealing challenge in the performance based tuning of the surface chemistry of construction materials that are based on cement. The durability has to be improved without impairing the mechanical strength or temperature resistance of the system. Toward these points, the inherent hydrophobization via ion exchange is far superior to that of conventional surface protection systems. The detailed knowledge from basic research acquired in this project can finally be transferred to industry for innovation. As depicted in Figure 1, the incorporation of new metals would be possible at different points during the production of cement bound material both before and after hydration.¹²⁴

CONCLUSION AND OUTLOOK

The goal of this work was to explore exchange reactions at mineral interfaces. The report focused on both natural mineral interfaces such as wollastonite and synthetic mineral interfaces. The use of model surfaces was key to bridging the gap between fundamental research and applied technologies. The presented model surfaces allow for the transfer of high performance analytical, theoretical, and experimental methods, which are

currently limited to academic samples, to the macroscopic scale. Particularly important interactions occurring on C–S and C–S–H surfaces are those with water and CO₂. Importantly, it has been found that hydroxyl formation and carbonaceous adsorption have opposite effects on organic molecules' ability to form chemical bonds with the oxide/hydroxide surface. Metal–proton exchange reactions (MPERs) are the rather complex processes that occur when minerals containing C–S or C–S–H phases contact environments containing water. In the cases of C–S and C–S–H, this process leads to the leaching of calcium from the near surface region, which is the first step in the corrosion of cement bound materials. The so called MPER appears to be the most important of the various corrosion reactions of C–S and C–S–H phases. The passivation of C–S–H surfaces is a promising approach to bridging certain problems caused by carbonation and MPER. One way to achieve such passivation is by using water repelling films to functionalize C–S–H surfaces. ODPAs are among the molecules that can bind with hydrated cement. The formation of calcium alkoxides, which has been generally neglected in previous studies, needs to be considered when applying nanolime (alcoholic dispersions of Ca(OH)₂ nanoparticles) treatments for the conservation of cultural heritage. Nanolimes have emerged as effective conservation materials for consolidating plasters, stone, and mortars in old masonry and/or mural paintings.

Finally, the design of a new model system with high reproducibility, significance, and applicability was discussed. Ultrathin C–S–H and C–S phases have been designed on silicon wafers, allowing for many different applications in research and industry in the future. Prospective fields for research were illustrated. The development of several interface applications is made possible by the C–S–H and C–S phases on silicon wafers because of their unique chemistry in wastewaters and other elements that have to be recovered or urgently removed to avoid serious health problems, such as arsenates. These substrates might be promising materials as sensors for phosphates. New compounds that are important for the medical industry because of their bioactivity, such as calcium phosphates, can now be synthesized. A very feasible approach for semiconductor manufacturing would be the use of these substances for doping phosphorus into silicon wafers. It is relevant to catalysis research that calcium can be exchanged through other metals, such as nickel. Successfully developing applications is dependent on the reproducibility and accuracy of the future production of these substrates. Finally, the scientific fields of carbon capture and storage or nuclear waste storage greatly depend on mineral–fluid interactions. MPER and MMER will play key roles in understanding fundamental processes, designing new materials, and developing new methods for minerals.

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Notes

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Biography

Peter Thissen studied chemistry in Essen, Germany. Then he went to the Max Planck Institut für Eisenforschung in Düsseldorf. After receiving his Ph.D. in 2009, he was awarded his first DFG grant and then was a postdoctoral researcher to Dallas, Texas. In 2013, he returned to Germany and became head of the model development of mineral interfaces group at the Karlsruhe Institute of Technology. He was awarded a Heisenberg Grant in 2018 for research on the combined mechanical and chemical interactions on cement bound materials. His research interests include mainly mineral interfaces such as silicates and carbonates, and he is a hybrid in combining both theoretical and experimental work.

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ABBREVIATIONS

C–S, calcium silicate; C–S–H, calcium silicate hydrate; MPER, metal–proton exchange reaction; MMER, metal–metal exchange reaction

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