AFM study of the interactions between moisture and the surface of cementitious materials

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AFM Study of the Interactions between Moisture and the Surface of Cementitious Materials

A dissertation submitted to the

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Doctor of Technical Sciences

presented by

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Prof. Dr. Karen Scrivener, co-examiner

2006
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Zusammenfassung

Das Ziel dieser Arbeit war die Untersuchung der Wechselwirkung der Luftfeuchtigkeit mit den inneren Oberflächen von Zement auf einer molekularen Skala. Dazu mussten zwei Probleme gelöst werden:

1. Es mussten die Hauptkomponenten von Zement: CSH (Calcium-Silikat-Hydrat) und Ca(OH)$_2$ so präpariert werden, dass sie atomar ebene Oberflächen aufweisen.
2. Es mussten die Untersuchungsmethoden des Rasterkraftmikroskops (AFM) so angepasst werden, dass damit molekulare Wasserfilme auf solchen Oberflächen untersucht werden können.


Die Probenpräparation konzentrierte sich auf die beiden Hauptkomponenten: CSH und Ca(OH)$_2$. Von letzterer konnte durch Aufwachsen auf atomar ebene Glimmerflächen hexagonale Kristallplatten mit atomar ebener Struktur erzeugt werden. Durch Exposition zu einer Atmosphäre mit kontrollierter Zusammensetzung: N$_2$, CO$_2$ und H$_2$O konnte gezeigt werden dass und wie der Karbonatisierungsprozess von Ca(OH)$_2$ einsetzt: Erst ab einer relativen Feuchtigkeit von 30% bilden sich molekulare Wasserschichten welche CO$_2$ lösen und so den Karbonatisierungsprozess bewirken.

Mit dem FIB (Focused ion beam) konnten Lamellen von annähernd atomarer Ebenheit herausgeschnitten werden. Leider wurde aber durch das Bombardement mit Ga-Ionen die Oberfläche wesentlich verändert: Amorphisierung und Implantation von Ga-Ionen. Deshalb wurde versucht, CSH aus CaCO$_3$ und Wasserglas Na$_2$SiO$_3$ zu züchten. Als Ergebnis erhält man zwar dünne Schichten (20nm) von CSH aber nicht atomar eben sondern mit einer
Zusammenfassung
Blumenkohl-ähnlichen Struktur. Auch das Nachvollziehen der Vorgehensweise einer Gruppe an der Universität Bourgogne (Dijon, France) ergab keine atomar ebenen Flächen mit CSH. Deren Proben, welche uns zur Verfügung gestellt wurden, zeigten überhaupt kein Si-Signal, so dass unserer Ansicht nach die behauptete Existenz von atomar ebenen CSH-Schichten in Frage gestellt ist.


Mit der vorliegenden Arbeit konnten so die Grenzen dieser Methoden auf Strukturen wie Zement aber auch einige interessante Nebenergebnisse betreffend Carbonatisierung aufgezeigt werden
Abstract

The work presented in this thesis attempts to study the interaction between moisture and cementitious material surfaces on a molecular scale by means of Atomic Force Microscopy (AFM). There are two key problems to be solved: 1) to prepare samples of cementitious materials with flat surfaces that are suitable for AFM studies on a molecular scale; and 2) to develop appropriate AFM imaging techniques which enable the visualization of moisture condensation and evaporation processes on the surfaces.

The AFM studies of the wetting phenomena on solid surfaces include morphology study and force measurement under controlled relative humidity (RH): 1) To avoid the interference due to a physical contact between the AFM tip and the water film, two AFM imaging modes are applicable, tapping mode AFM and another sophisticated AFM mode, Amplitude-Modulated Scanning Polarization Force Microscopy with Kelvin Probe Microscopy (AM-SPFM+KPM). In AM-SPFM+KPM, the nature of the long-range electrostatic force enables the detection of water molecular film on mica substrate; 2) The adhesion force between the AFM tip and the surface is studied with force-distance measurement at a selected position and with force-volume measurement over a selected area. The adhesion force as a function of RH is used to study the wetting property of the solid surface (hydrophilic and hydrophobic) at precisely defined positions (on nm scale).

The problem of sample preparation is focused on the principal cementitious material, i.e. hydrated cement paste. It consists of a complex mixture of different hydrate phases, of which the major components are represented by Ca(OH)$_2$ and Calcium Silicate Hydrate (C-S-H).
1) The hydrated cement paste was prepared by casting samples against freshly-cleaved mica. It produces flat surfaces of Ca(OH)$_2$. The surface nano-structure was characterized directly by contact mode AFM under controlled atmospheres. Thereby, carbonation processes of Ca(OH)$_2$ could be observed in real-time. Ca(OH)$_2$ is transformed to CaCO$_3$ only if CO$_2$ and H$_2$O are simultaneously present and if the RH exceeds 30%;
2) Focused Ion Beam (FIB) milling technique was applied to polish flat surfaces and to prepare thin lamella. The FIB-prepared thin lamella enables high resolution Energy Dispersive X-ray (EDX) analysis. However, FIB-preparation leads to a considerable modification of the surface structure (amorphization) and composition (Ga-implementation);
Abstract

3) Experiments were repeated to reproduce atomically flat C-S-H micro-domains, following the procedures as described by a group at University of Bourgogne (Dijon, France), whereby freshly-cleaved calcite (CaCO3) reacted in a concentrated water glass (Na2SiO3) solution. Instead of atomically flat micro-domains of C-S-H, this method produced a thin layer (20nm) of C-S-H coverage on the calcite substrate, showing a ‘cauliflower’-like structure. Examinations on their samples (which were present for our test) showed that the flat surface are not C-S-H, since no Si signal is detected in EDX analysis.

4) Nano-manipulators were used to separate individual tobermorite crystals from Autoclaved Aerated Concrete (AAC) in Environmental Scanning Electron microscope (ESEM). The surface nanostructure and its interaction with moisture were studied with the above-mentioned AFM techniques. The surface turns out to have hydrophobic characteristics and no water molecular films on tobermorite surfaces were observed. The hydrothermal experiments didn’t succeed in re-hydroxylation of the surface.

AFM studies of the wetting process on 3 solids surfaces show mica and Ca(OH)2 crystal to be hydrophilic while tobermorite to be hydrophobic. From the viewpoint of surface chemistry (crystal structures and chemical compositions), these 3 solids surfaces are all hydrophilic and can form hydrogen bonding with water molecules. The abnormal result of tobermorite is possibly due to the artifacts induced by the electron beam bombardment in ESEM. For future wetting experiments on cement surfaces, it is of essential importance to prepare samples with verified chemical compositions and to avoid the artefacts produced by electron or ion beam.
Chapter 1 Introduction

1.1 Motivation

The combined transport of heat and moisture in porous building materials plays an important role for the durability of materials and the sustainability of construction, and more important energy consumption in buildings. In almost any porous material water is transported by at least three processes (in the range of moisture content normally encountered):

- direct vapour diffusion;
- capillary transport;
- water film transport on the internal surfaces.

The three processes interact and are in a dynamic balance with the surfaces involved [1]. These processes are thus principally determined by the pore structure as well as the surface area and states of water. They are also correlated with the engineering properties of the materials, such as strength, modulus of elasticity, volume changes and permeability [2, 3].

In the hardened cement paste, pore structure and surface area are determined using surface chemical techniques with gases or vapors, such as N₂, He, H₂O and CH₃OH [4]. To interpret the data correctly, one should be aware of their limitations. On one hand, before surface areas can be measured, all the gas molecules have to be removed from the surface. This usually takes both heat and vacuum. Hydrated Portland cement is, however, unstable both chemically and structurally under such conditions. An example of its structural instability is the irreversible shrinkage on first drying from a saturated state [4]. On the other hand, the correct interpretation also depends on the knowledge about the moisture adsorption process on the inner surface. It needs to be determined under which condition (humidity and temperature) the mono- or poly-molecular layer builds up on the surface [3, 5].

It has been the goal of this thesis to understand the interaction between moisture and surfaces of cementitious materials on molecular level. To this end, two key problems have to be solved:

- to prepare the sample of cementitious materials with flat surfaces for AFM studies on the molecular scale;
- to visualize the moisture condensation and evaporation processes on the solids surfaces with appropriate AFM imaging techniques.

The rest of this chapter will review the literature about cementitious materials and briefly describe AFM imaging techniques and chemical composition analysis.
1.2 Hydrated Portland cement paste

The reaction of anhydrous Portland cement with water produces a complex mixture of several compounds, all hydrates, which yields a structure with strength called hydrated cement paste.

1.2.1 The state of water in cement paste

The role of the various states of water is important in understanding the behaviour, structure and chemistry of hydrated Portland cement paste. In the literature, different terms are used to describe the states of water. Since the pores range in size from macroscopic to interlayer spaces of nanometre dimensions, the water content can be defined only in relation to a specific drying condition. Basically there are three states of water [6], related to the pore structure and drying conditions (Table 1.1):

- I. Physically adsorbed water (free water, or capillary water);
- II. Chemically bound water in interlayer spaces;
- III. Chemically bound water at Si-tetrahedra or Ca-octahedra (‘Non-evaporable’ water).

Table 1.1 The relation of the water states to the pore structure and drying conditions

<table>
<thead>
<tr>
<th>Drying conditions</th>
<th>Pore structure filled by water</th>
<th>Water states</th>
<th>Water content (wt%)</th>
<th>Water content in C₃S paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated</td>
<td>Microscopic to macroscopic</td>
<td>I+II+III</td>
<td>42-44%</td>
<td>1.7CaO·SiO₂·4H₂O</td>
</tr>
<tr>
<td>11%RH equilibrium</td>
<td>Interlayer space</td>
<td>II+III</td>
<td>32%</td>
<td>1.7CaO·SiO₂·2.1H₂O</td>
</tr>
<tr>
<td>D-drying</td>
<td>Non-evaporable</td>
<td>III</td>
<td>20.4-22%</td>
<td>1.7CaO·SiO₂·1.3-1.5H₂O</td>
</tr>
</tbody>
</table>

Saturated condition: The pores are totally filled with water.
D-drying: Equilibration at the vapour pressure of dry ice, -79°C, $P_{\text{water}}=6.67 \times 10^{-2}$ Pa [7].

The water content is usually measured in terms of the amounts of water held either at various vapour pressures with constant temperature (“isotherm”), or at various temperatures with constant pressure (“isobars”) [2].

1.2.2 Chemical composition and morphology of cement paste

The chemical and physical properties of cement paste are complicated not only by the varied morphology, but also by the wide variability of the chemical compositions (Ca/Si ratio, water
Chapter 1

Table 1.2 briefly summarizes the main components of the hydrated cement paste. The most important hydrate is the very poorly crystalline calcium silicate hydrate known as C-S-H, or C-S-H gel. It is compositionally variable with respect to ratios of calcium, silicon and hydrogen on the atomic scale, bearing some similarity to a naturally occurring class of minerals called tobermorite and jennite.

The development of microstructure during the hydration of Portland cement has been extensively investigated by Scrivener [8] using electron optical techniques and calorimetry. The mechanism of cement hydration is described as in Fig. 1.1 to understand the development of the inner and outer product gel. Four morphological types of CSH gel have been identified and named types I to IV [9].

The average Ca/Si ratio of C-S-H gel in a hardened cement paste is around 1.7. The local Ca/Si ratio varies. The data are scattered due to various causes, such as starting materials (C₃S, C₂S, cement clinker), reaction time, temperature, water/solid ratio, particle size distribution, and so on. Even in one sample, the Ca/Si ratio shows significant fluctuations in different areas of interest (‘inner product’ and ‘outer product’) [10, 11].

Fig. 1.1 Microstructure development during the hydration of Portland cement, after Scrivener [8].
### Table 1.2 The main components in the hydrated Portland cement paste [6, 12-16]

<table>
<thead>
<tr>
<th>Main components</th>
<th>Chemical composition</th>
<th>Morphologies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C-S-H gel</strong></td>
<td>CaO-SiO$_2$·nH$_2$O</td>
<td>prominent at early stages of hydration, more open, structured and porous morphologies:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Type I: fibrous, up to 2 µm in length, &lt;0.2 µm across;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Type II: honeycomb or reticular structure.</td>
</tr>
<tr>
<td><strong>Calcium</strong></td>
<td>Ca(OH)$_2$</td>
<td>prominent in older pastes:</td>
</tr>
<tr>
<td>Hydroxide</td>
<td>(portlandite)</td>
<td>• Types III, more massive and appears to consist of tightly packed equant grains up to 300 nm across;</td>
</tr>
<tr>
<td><strong>Calcium</strong></td>
<td></td>
<td>• Type IV, still more featureless and massive.</td>
</tr>
<tr>
<td>Aluminoferite</td>
<td>[Ca$_3$(Al,Fe)(OH)$_6$·12H$_2$O]$_2$·X$_3$·nH$_2$O</td>
<td>thin hexagonal platelets</td>
</tr>
<tr>
<td>hydrate</td>
<td>(AFt phase)</td>
<td>Ettringite is the most important AFt phase: prismatic or acicular, slender needles</td>
</tr>
<tr>
<td><strong>Calcium</strong></td>
<td>CaSO$_4$·nH$_2$O,</td>
<td>Tablets or prisms</td>
</tr>
<tr>
<td>Sulfate hydrate</td>
<td>Gypsum</td>
<td></td>
</tr>
</tbody>
</table>

$X$ represents one formula unit of a doubly charged, or two formula units of a singly charged anion, such as SO$_4^{2-}$, CO$_3^{2-}$, OH$^-$. 

### 1.2.3 Structural models for the C-S-H

The structure of C-S-H is poorly determined partially due to compositional and structural complexities and partially due to poor crystallinity. The development of the structural model for C-S-H has historically relied on postulates based on indirect experimental evidence [3]. The most well-known models of C-S-H structure include [3, 6]: Powers-Brownyard model, Wittmann model, Feldman-Sereda model (F-S model), and Taylor model. Taylor and F-S models appear to be supported by the largest body of experimental evidence of the most important analytical and physiochemical properties of C-S-H gel. F-S model [4] is shown in Fig. 1.2. It can be used to explain the humidity dependence of the mechanical properties of hardened cement paste, eg. strength and modulus of elasticity.
F-S model was further developed by Taylor by combining it with the hypothesis that most of the layers are structurally imperfect ones of jennite (C-S-H(II)) and a smaller portion are similarly related to the of 1.4-nm tobermorite (C-S-H(I)) [17]. In contrast, Cong’s model focuses on the similarity and importance of tobermorite to C-S-H [18, 19]. Lesniewska and Lecoq [20, 21] proposed a slightly different model: the layers don’t contain jennite-like regions, that is, calcium in the main plane would not coordinate to OH⁻. Each missing bridging tetrahedral makes available two crystallographic sites for OH⁻ and Ca(OH)₂ units.

Fig. 1.2 Feldman-Sereda model of the structure of the C-S-H gel shows: C-S-H layers (lines), interlayer water molecules (crosses) and adsorbed water molecules (circles) [4].

It is difficult to have one model to precisely represent all the observed properties and structure of C-S-H in cement paste. However, it is commonly accepted that the C-S-H is a layered structure, which is built up by the three distinct modules:

- Silicate anion chain structure made of the repetition of a pattern of three tetrahedra ("dreierketten");
- Ribbons of edge-sharing calcium octahedral;
- Interlayer water and / or calcium ions.

Silicate anion chain linked to the ribbon of edge-sharing calcium octahedral chain via the paired silicate tetrahedra. These two chains form the main layer. The interlayer between the main layers is occupied by sevenfold coordinated calcium polyhedra and excess water; the latter gives rise to the difference in basal spacing between the tobermorites. An example of the layer structure is shown in Fig. 1.3 for 1.1nm-tobermorite [22]
1.2.4 Silicate anion structure

The silicate chains are kinked to repeat at intervals of three silicon tetrahedral, known as ‘dreierketten’ (Fig. 1.4) [6]. Two of the three tetrahedra share O atoms with the Ca-O layer (paired tetrahedral), but the third does not and is referred to as a bridging tetrahedron; repeating distance of 7.3Å along the $b$-axis. If some or all of the bridging tetrahedra were missing, finite chains containing 2, 5, 8, ...3n-1 tetrahedral would result. The bridging tetrahedron has its silicon atom positioned either above or below the two paired tetrahedra, but always pointing into the interlayer. Such a structure can be used to explain the various Ca/Si ratios of the C-S-H, by a combination of omission of tetrahedral from the chains and incorporation of additional calcium in the interlayer. The structural features of tobermorite and jennite minerals are given as two examples of the layer structure.
1.2.5 Tobermorite and jennite

The structure features of tobermorite and jennite minerals are given as two examples of the layer structure, as described in Table 1.3.

Table 1.3 The idealized structure of tobermorite and jennite [22-29]

<table>
<thead>
<tr>
<th>Minerals</th>
<th>1.4nm-Tobermorite</th>
<th>Jennite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Side</td>
<td>Si$_3$O$_9$H dreierketten chain</td>
<td>Si$_3$O$_9$H dreierketten chain</td>
</tr>
<tr>
<td>Central</td>
<td>Ca-O octahedral zigzag chain</td>
<td>Ca-O octahedral chain</td>
</tr>
<tr>
<td>Side</td>
<td>Si$_3$O$_9$H dreierketten chain</td>
<td>OH groups</td>
</tr>
<tr>
<td>Interlayer</td>
<td>H$_2$O + Ca$^{2+}$</td>
<td>H$_2$O + Ca$^{2+}$</td>
</tr>
</tbody>
</table>

Idealized chemical composition:

- Tobermorite: [Ca$_4$(Si$_3$O$_9$H)$_2$]Ca·8H$_2$O
- Jennite: [Ca$_8$(Si$_3$O$_9$H)$_2$(OH)$_8$]Ca·6H$_2$O

Different phases and layer thickness:

- Tobermorite: 1.46nm – T $\rightarrow$ 1.13nm – T $\rightarrow$ 0.93nm – T
- Jennite: Jennite $\rightarrow$ Metajennite

Recent results suggest that the crystal chemistry is Ca$_9$Si$_6$O$_{18}$(OH)$_6$·8H$_2$O for jennite, and Ca$_9$[Si$_6$O$_{16}$(OH)$_2$](OH)$_8$ 2H$_2$O for metajennite [28].

1.3 Atomic Force Microscopy (AFM)

AFM imaging technique has many prominent features: 1) high spacial resolutions and versatility; 2) digital three-dimensional morphological information; 3) measurements under different environmental, no vacuum requirements; 4) real-time imaging during reaction; 5) high sensitivity in surface forces (in pN) [30-35]. Many kinds of microscopy have been developed to various operation modes. Table 1.4 summarises the AFM modes used in this work. The specifications of the instruments are given in Table 1.5.

The AFM is seated in a glove-box flushed by N$_2$ and with controlled RH, measured by a dew-point hygrometer (Bruel & Kjar, Indoor Climate Analyzer Type1213, humidity transducer MM0037) with an accuracy of dew point of 1°C.
Table 1.4 AFM operation modes used in this work

<table>
<thead>
<tr>
<th>Mode</th>
<th>Feedback signal</th>
<th>Remarks (resulting images and its sensitivity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact mode</td>
<td>Cantilever bending</td>
<td>• Topographical resolution depends on tip-sample contact area, typical contact diameter=1-10nm;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• No true atomic resolution (single point defects), but images of the atomic lattice;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Effects of lateral force (scratching): Artefacts coupled in height images.</td>
</tr>
<tr>
<td>Tapping mode;</td>
<td>Oscillation amplitude</td>
<td>• Temporarily in contact with surface;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Eliminates the lateral force effect.</td>
</tr>
<tr>
<td>AM-SPFM+KPM*</td>
<td>Oscillation amplitude; 2 loops</td>
<td>• Tip is far away (&gt; 10 nm) from the surface to minimize the perturbation of delicate liquid surfaces;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Decreased resolution in the xy plane (100nm), while angstrom level in the z-direction.</td>
</tr>
<tr>
<td>Force-distance curve</td>
<td>Feedback off</td>
<td>• Images: Surface forces; Force mapping; Topography;</td>
</tr>
</tbody>
</table>

* AM-SPFM+KPM = Amplitude-modulated Scanning Polarization force Microscopy and Kelvin Probe Microscopy

Table 1.5 AFM instruments and their specifications

<table>
<thead>
<tr>
<th>Instruments</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q-250 (Quesant Inc.)</td>
<td>40 µm scanning head (See chapter 2)</td>
</tr>
<tr>
<td>AFM Multimode (Veeco Instruments Inc.)</td>
<td>Nanoscope IV controller; 10 µm scanning head (See chapter 3 &amp; 4)</td>
</tr>
<tr>
<td>AFM tips</td>
<td>Model</td>
</tr>
<tr>
<td>Contact mode, CSC17, Si</td>
<td>460</td>
</tr>
<tr>
<td>Contact mode, OTR8-35, Si3N4</td>
<td>200</td>
</tr>
<tr>
<td>Tapping mode, RTESP7, Si</td>
<td>125</td>
</tr>
<tr>
<td>SPFM, SCM-PIT, Si + Pt-Ir</td>
<td>225</td>
</tr>
</tbody>
</table>

1.4 Literature review on the application of AFM in cementitious materials

The application of AFM in the research field of cement and concrete is limited, mainly due to the following facts:

- In AFM imaging, the tip is in mechanically contact (contact mode) or near contact (tapping mode or non-contact mode) with the sample surface to keep the necessary
tip-surface interactions. This requires the surface to be reasonably flat. Too rough surface with high corrugations (several µm) will lead to the crash of tip or sample, or the lost tip-sample contact;

- To achieve high resolution in the AFM imaging, it is essential to reduce the interaction area between the tip and the surface. In contact mode, the observation of atomic features is limited to the imaging of the lattice. Single point defects have not been observed so far. This lack of true atomic resolution in contact mode is explained by the fact that the area of the tip-sample contact is larger than atomic dimensions. Typical contact diameters in contact mode force microscopy lie in the range 1-10 nm, limiting the lateral resolution. Non-contact AFM is currently the only operation mode providing true atomic resolution and images of a quality comparable to STM[31, 33];

- AFM lacks the direct chemical composition identification of the surface materials. Surface regions of different compositions will change the tip-surface interactions, which induce the contrast in the AFM images (phase images, friction force or adhesion force images) between these regions. This contrast can only be understood when the compositions of the surface regions are known.

The cement and concrete are porous materials with complicated structures and chemical compositions, as discussed in the previous sections. It is difficult to directly investigate the natural state of such materials using AFM. However, efforts have been made to apply AFM as a tool for topography and force measurements. The high resolution surface structure observed directly by AFM in non-vacuum condition provides important information to understand the properties of cementitious materials.

As early as 1992, Uchikawa et al[36] used AFM to observe the organic admixture adsorbed on the surface of alite and its influence on the early age hydration of cement clinker and thus the setting time. They also proved for the first time the existence of the steric repulsive force acting on the surface of cement particles adsorbing the organic admixture by measuring the interactive force between surface of cement clinker adsorbing the admixture with an AFM[37]. Since then, AFM was exploited to study the real-time process of the early hydration of C₃S and cement[20, 38-42], surface structure of clinotobermorite[43], fly ash topography and its effect on cement paste microstructure [44-51], silica fume[52], environmental particles[53-55], atmospheric aerosols[56], gypsum crystal[57-59], surface chemical reaction on Ca(OH)₂ crystals (carbonation)[15, 16], morphology of Ca(OH)₂ passive film grown on stainless steel[60], calcite crystal surface[61-65], surface corrosion resistance and primary fracture-
causing defects of the Alkali-resistant glass fibers reinforcements[66], polymer admixture in cementitious matrix[67].

The AFM force measurements are used to study the surface forces between the C-S-H to reveal the origin of the cement cohesion (Nonat and coworkers [68-70] and Pellenq et al[71, 72]) , effect of superplasticizer adsorption on surface[73], the elastic properties of C-S-H at nanoscale by nano-indentation[21], correlation between surface forces and surface reactivity in the setting of plaster[74-77].

In the literature of the above-mentioned AFM applications, the limitations of AFM are circumvented in the following cases:

- Model materials (Ca$_3$SiO$_5$, gypsum, Ca(OH)$_2$, MgO, et al) are studied to give some hints in understanding the structure and properties of cement and concrete;
- Topography are studied when the nm resolution is not required;
- AFM studies are often combined with other surface characterization techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDX), nuclear magnetic resonance (NMR), single-particle X-ray diffraction, and so on.

To better apply AFM studies on the nature of cement and concrete, special sample preparation techniques need to be developed. Lesniewska and coworkers have developed some sample preparation techniques to study the C-S-H by AFM. The early hydration of C$_3$S particle and the growth of C-S-H in wet conditions was observed by AFM. Some globules of C-S-H with typical sizes of 60x30x5 nm were found[40, 41]. They also prepared flat form of C-S-H on substrate of silica glass and calcite surfaces through chemical reactions. In the case of the C-S-H coverage onto the calcite crystals, a long equilibrium time allowed partial recrystallization, which produced atomically flat areas (micrometric domains). On such areas, atomic resolution of the surface was revealed, which made possible the investigation of C-S-H cell surface parameters[20, 21, 69, 70]. By producing a C-S-H coverage on the AFM tip, the interaction between the C-S-H was measured more precisely with reduced influence of the roughness effect. Different electrolytic solutions were used to determine influent parameters. It was found out that the cohesion of cement paste originates from ionic correlation force of electrostatic nature[69].

We tried to reproduce the synthesis of C-S-H with the atomically flat micrometric domains as described by Lesniewska and coworkers. They provided some of their samples for our test. The results are presented in chapter 3.
1.5 Chemical composition analysis

The chemical composition of the samples was analyzed by the surface chemistry analysis techniques, as summarized in Table 1.6.

Table 1.6 Surface chemistry analysis techniques

<table>
<thead>
<tr>
<th>Methods</th>
<th>Instruments and specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESEM-EDX</td>
<td>Philips ESEM-FEG XL30</td>
</tr>
<tr>
<td></td>
<td>low vacuum condition or wet mode;</td>
</tr>
<tr>
<td></td>
<td>Sample without conductive coatings.</td>
</tr>
<tr>
<td>TEM-EDX</td>
<td>FEI, CM30, source LaB6</td>
</tr>
<tr>
<td></td>
<td>Digital Micrograph (Ver. 3.9, Gatan Inc.)</td>
</tr>
<tr>
<td></td>
<td>bright field scanning mode;</td>
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<tr>
<td></td>
<td>accelerating voltage: 200 kV.</td>
</tr>
<tr>
<td>LA-ICP-MS[78]</td>
<td>Laser: 193 nm ArF excimer laser with pulse repetition rate of 1Hz</td>
</tr>
<tr>
<td></td>
<td>and energy of 60 mJ (5 J/cm²), diameter 20 microns.</td>
</tr>
<tr>
<td></td>
<td>Ablated materials was analysed with an inductively coupled plasma mass</td>
</tr>
<tr>
<td></td>
<td>spectrometer (ICP-MS).</td>
</tr>
</tbody>
</table>

ESEM = Environmental Scanning Electronic Microscope;
TEM = Transmission Electron Microscope;
EDX = Energy-Dispersive X-ray analysis;
LA-ICP-MS = Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry[78];
Chapter 2 Direct observation of carbonation on the surface of Ca(OH)$_2$ crystals in hardened cement paste using AFM

2.1 Carbonation of calcium hydroxide in cement paste

Calcium hydroxide, Ca(OH)$_2$, is one of the main reaction products resulting from the hydration of Portland cement with water. It has a major significance for the mechanical properties of the most important building material, the reinforced concrete. Ca(OH)$_2$ layer forms a protecting chemical screen against the corrosion of its reinforcement. The main danger for the chemical stability of CH in concrete is its carbonation process. As a consequence of the gradual carbonation of CH, the alkaline screen protecting the reinforcement disappears and the corrosion sets on\[6, 12\].

In the literatures\[79-85\], different experimental techniques as Transmission Electron Microscopy (TEM), Nuclear Magnetic Resonance (NMR), Scanning Electron Microscopy (SEM), Differential Thermogravimetry (DTG), etc. were used. The carbonation process is known to proceed from the surface into the paste at a rate controlled by gas diffusion through the pores. The reaction occurs with carbon dioxide in aqueous solution and the rate of reaction depends strongly on the water-cement-ratio of the paste and the relative humidity (RH) of the atmosphere, which reaches a maximum at intermediate values of RH (50%-70%)\[79-85\]. In most of the cases, the samples were exposed for a certain time to the influence of a controlled atmosphere, such that on the real-time development of the carbonation process little detailed information is available. This is largely because of the requirements of sample preparation techniques and the mentioned experimental methods which prevent a direct on-line observation of the reactions. In addition, in the electron microscopy several basic difficulties such as the limit of spatial resolution, the loss of focal depth on curved surfaces with increasing magnification, the masking effect on fine structure of a conductive coating etc. are encountered.

This chapter presents the direct AFM observation of the real-time carbonation process of Ca(OH)$_2$ crystal surface in hardened cement paste at nanometer scale.
2.2 Sample preparation: Mica-Replication-Method (MRM)

The mixture of Portland cement powder with distilled water (water/cement ratio of 0.4 in weight) was cast on a freshly-cleaved mica and stored in a sealed container (100% RH) for 28 days. The pastes were then dried in pure N₂ (99.995%) and removed from mica due to the stresses produced by the shrinkage [13, 15, 16].

2.3 Surface chemical composition analysis

The LA-ICP-MS spectra show signals of Ca44, Ca 42 and Ca43. No signals of of Si28, Si30, S32, Al27, K39, Si29, Mg24, Mg25, Na23, Fe57 were detected. The layer depth of one laser ablation is about 400nm, as measured by AFM. In the EDX-analysis spectrum, only Ca and O are detected (Fig. 2.1). Both LA-ICP-MS and EDX analysis results show the flat surface of MRM prepared cement paste to be Ca(OH)₂.

![Fig. 2.1 Signal-time spectra of LA-ICP-MS analysis (left) and ESEM-EDX analysis (right) of the MRM prepared cement paste surface.](image-url)
Chapter 2

2.4 Nanostructure of CH surface in different atmospheres

The MRM prepared cement paste was heated to 150 °C for 2 hours to dry the sample without water condensation on surface. The surface was studied by AFM under different atmospheres: (i) N$_2$+H$_2$O, (ii) N$_2$+CO$_2$ and (iii) N$_2$+CO$_2$+H$_2$O atmosphere, respectively.

2.4.1 In atmosphere of N$_2$+CO$_2$ (flow ratio of N$_2$/CO$_2$ is 10:1)

No apparent changes of surface structure were found after two days (Fig. 2.2).

2.4.2 In atmosphere of N$_2$+H$_2$O (RH ranges from 3% to 41%)

At lower RH (<30%), the surface shows a smoothing effect and the main structure remains unchanged (the step height in the center of image remains at about 13nm). At higher RH (>41%), no stable image was obtained with the contact-mode AFM. The surface seems to be dissolved by the water film from moisture condensation (Fig. 2.3).

2.4.3 In atmosphere of N$_2$+CO$_2$+H$_2$O (RH ranges from 3% to 50%)

At lower RH (< 30%), the surface structure remains unchanged. At 30%RH, particles with size of about 160x160x23nm were found on the surface (Fig. 2.4). Some of the particles are movable under the scanning tip, while others are fixed (Fig. 2.5). The particle’s size grew from 160x160x23nm to 260x260x42nm under this atmosphere at 30%RH (Fig. 2.4). The new phase starts to grow on the Ca(OH)$_2$ surface only when both CO$_2$ and H$_2$O are simultaneously present and when the moisture content is increased to a certain level (30%RH). The condensation of moisture forms a water film or nano-droplets on the surface. The gaseous CO$_2$ is dissolved in the water nano-droplets to form aqueous H$_2$CO$_3$, providing favourable conditions for the carbonation of the Ca(OH)$_2$.

After long term (> 1 year) exposure in ambient air (N$_2$+O$_2$+H$_2$O+CO$_2$), the surface was covered with a layer of spherules (Fig. 2.6).

With the aid of the AFM, the process of Ca(OH)$_2$ surface carbonation could be monitored directly and followed in real time. Moisture plays the key role.
Chapter 2

Fig. 2.2 AFM image of the CH crystal surface in N₂ + CO₂ atmosphere

Fig. 2.3 CH crystal surface changes with RH in N₂ + H₂O atmosphere.
Fig. 2.4 CH crystal surface structure changes with RH in N$_2$ + CO$_2$ + H$_2$O atmosphere

Fig. 2.5 Movable spherules grow on CH surface in N$_2$+CO$_2$+H$_2$O atmosphere at 30% RH: first scan (left), second scan (middle) and after several scan (right) with AFM in full contact mode.
Fig. 2.6 AFM image of cement paste exposed to the ambient air for more than one year.
Chapter 3 Preparation of calcium silicate hydrate (C-S-H)

Direct AFM study on the poorly crystalline C-S-H in the cement paste is limited due to the difficulties as discussed in chapter 1. Special sample preparation techniques are needed. In this chapter, three methods to prepare the AFM sample of C-S-H are discussed:

1) To reproduce the atomically flat form of C-S-H as described by Lesniewska and coworkers [20, 21, 69, 70, 86]: chemical synthesis method via the reaction of freshly-cleaved calcite (CaCO$_3$) crystal in the concentrate sodium silicate solution;
2) Focused ion beam (FIB) milling technique is applied to polish the surface;
3) Single tobermorite crystals are separated from the autoclaved aerated concrete (AAC) by using nano-manipulator.

3.1 AFM study of calcite crystal surface

The freshly-cleaved calcite surface shows atomically flat terraces with steps of about 0.3nm (Fig. 3.1). Moisture condensation forms water films on the surface and calcite surface dissolves. When saturation is reached, the dynamic equilibrium triggers the spontaneous recrystallization and new calcite precipitates on the surface, in monolayer-high bumps on terraces (Fig. 3.1).

3.2 C-S-H produced by chemical synthesis

The freshly-cleaved optical quality calcite was immersed in the concentrate sodium silicate solution (Rm=[SiO$_2$]/[Na$_2$O]=0.33, [SiO$_2$]=0.5mol l$^{-1}$, pH=14.2). The reactions are [69]:

1. the calcite crystal dissolves into the solution and produce the calcium ions;
   \[ CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \]  \hspace{1cm} (1)
2. the dissolved calcium ions react with the SiO$_4^{2-}$ to produce C-S-H.
   \[ xCa^{2+} + H_2SiO_4 + 2xOH^- \rightarrow C - S - H \]  \hspace{1cm} (2)

The reactions were stopped by rinsing with de-ionized water or alcohol and drying with N$_2$.

3.2.1 Surface morphology of the reaction product

The surface nano-structure of the reaction products was studied in tapping mode AFM:
1) After 5 minutes’ reaction, some rhombohedral etched pits as well as nanosized particles were recognized on the calcite substrate. As reaction proceeds, the surface was covered with denser nanoparticles and the etched pits become deeper (Fig. 3.2a-c);

2) At longer than 2 hours, the surface was fully covered by the nano-particles as a layer product (Fig. 3.2d);

3) At 5 hours, some domains of several hundreds of nm size were observed on the previous homogenous nanoparticle layer. Such domains grew both in x-y direction and the z-direction (Fig. 3.2e);

4) Longer time (1 day to 30 days) of reaction developed surface structure of regular patterns of micro-domains covered with nano-spherules (Fig. 3.2f-h);

5) If the reaction was stopped by rinsing with water, the surface shows a uniform structure, like cauliflower: regular patterns of micro-domains and pores between the domains. The surface was covered with a nano-spherular structures (with sizes of around 100nm in lateral, and tens of nm in height) (Fig. 3.3);

6) If the reaction was stopped by rinsing with alcohol, the surface nano-structure showed a multi-morphology: Some micro-domains were covered by spherular structure; Other micro-domains showed flat surfaces with nanometric steps. Among the micro-domains, some continuous gel-like structures were also found (Fig. 3.3).

Fig. 3.1 Contact mode AFM image of the freshly-cleaved calcite shows the atomic steps of around 0.3nm (upper row); Tapping mode AFM images of the calcite crystals surface in the humid air (50%RH) at: a) 0 min; b) 10 min; c) 20 min after the cleavage.
Fig. 3.2 Tapping mode AFM images of the reaction production layer on calcite substrate at different reaction time, a) 5min; b) 30 min; c) 60min; d) 120min; e) 5 hour; f) 1day; g) 3 days and h) 7 days.
3.2.2 Chemical composition of the samples rinsed with water and alcohol

The EDX spectra in Fig. 3.4 show the chemical compositions of the samples. In the present EDX experimental conditions, the radius of the volume of interaction is around 1-2 µm. The results indicate:

- The layer of the reaction product is possibly very thin (small Si signal);
- When the reaction is stopped by rinsing with water, no Na is detected above the noise level. No water glass solution remains on the surface due to its high solubility;
- When the reaction is stopped by rinsing with alcohol, the sample contains Na and the semi-quantitative analysis shows the ratio of Na₂O:SiO₂ to be around 1:1. The remanent water glass deposits on the surface and solidifies in the drying process due to its low solubility in alcohol.

The results also explain the different nano-structures of the surface observed in the AFM studies (Fig. 3.3).
3.2.3 FIB prepared lamella and the EDX analysis

To understand the small signal of Si in ESEM-EDX spectra, a cross-sectional lamella (around 100nm thick) was prepared using the FIB milling technique for TEM-EDX analysis (Fig. 3.5).

- Pt and Au are the protective coating deposited before the FIB milling. Cu is from the TEM grid and Ga from the implantation of ion beam (Fig. 3.5d);
- A clear transition zone between Pt coating and Calcite substrate is seen both in the profile (Fig. 3.5e) and in the TEM image (Fig. 3.5c, the brighter Pt/Au coating, the darker calcite area and the very thin layer in between);
- The resolution of the TEM-EDX analysis is around 20nm, estimated from the slope of the Pt signal in Fig. 3.5e and the diameter of the bright trace in Fig. 3.5c). FIB efficiently improves the resolution of the EDX analysis.

No Na-signal is detected. The narrow peak of Si-signal as a function of the position confirms the reaction product layer to be very thin (around 20nm, at the limit of the TEM-EDX resolution).
Fig. 3.5 FIB milling technique to prepare the cross-section lamella and TEM-EDX analysis. a) top-view and b) side-view of the lamella (52°); c) TEM image of the lamella at position marked in b); d) EDX spectrum at one position; e) signal intensity of Pt, Ca and Si profile along the line indicated in c).
3.3 Modified synthesis method of C-S-H

The previous method of preparing C-S-H didn’t produce the atomically flat surface. With the help of Dr. Lesniewska [20, 21, 69, 70, 86], it was modified in the following procedures:

1. The freshly-cleaved calcite crystal was immersed into the concentrated sodium silicate solution (Rm=[SiO$_2$]/[Na$_2$O]=0.33, [SiO$_2$]=0.5mol l$^{-1}$, pH=14.2) in N$_2$ atmosphere. The containers were sealed and kept at 23 °C for one week;

2. Chemical synthesized C-S-H powder was added into the Ca(OH)$_2$ solutions with concentration of 2, 4, 10 mmol/l. The solutions were filtered after one week of equilibrium at 23 °C;

3. The reacted calcite samples were then immersed in the C-S-H saturated Ca(OH)$_2$ solutions for one month at 23 °C.

4. The samples were rinsed with alcohol and dried with N$_2$.

3.3.1 Topography studies with AFM

The surface nano-structure of the reaction products was studied with contact mode and tapping mode AFM in a glove-box filled with N$_2$.

Fig. 3.6 shows the topography of the reaction product on the calcite substrate with tapping mode AFM. The surface shows ‘cauliflower’ structure with micro-domains and pores covered with nano-spherules, similar to the results in previous experiment in section 3.2. Similar surface structures were found in all the samples which had been stored in the 3 different Ca(OH)$_2$ solutions.

When AFM was operated in contact mode, the imaging was not stable and the images showed black-and-white stripes, which corresponded to instable AFM tip-sample contact (Fig. 3.7). The possible reasons are 1) very big adhesion force between the AFM tip and the surface and 2) poor adhesion of the particles to the substrate. These were found in the experiments: The adhesion force between the AFM tip and the C-S-H on calcite sample (11.52nN) is twice as big as that on the freshly-cleaved mica surface (5.29nN), using the same AFM tip (Fig. 3.7).

In contact mode AFM, the scanning tip scratches the surface and removes away the poorly adhered particles (Fig. 3.8). After some continuous scanning, the stable images were obtained and the surface looked ‘clean’. On the locations where particles were removed, micro-domains with atomically flat surfaces were found.

The nano-structure of the flat surface changed with the scanning, as shown in Fig. 3.9. In Fig. 3.9d, the surface shows layer structure with thickness of 0.3nm, which is around one atomic
layer of calcite. The other parts of the particles were strongly adhered to the surface and were not removed, which showed the spherular structure.

This artefacts of contact mode AFM imaging were found in all the samples which had been stored in the 3 different Ca(OH)$_2$ solutions.

![Fig. 3.6 Tapping mode AFM images of the reaction production layer on calcite.](image)

![Fig. 3.7 Contact mode AFM image of the prepared C-S-H on calcite sample (left). Force – distance curves on mica surface and C-S-H sample using the same AFM tip (right).](image)
Fig. 3.8 In contact mode AFM, the tip scratches the surface and removes poorly adhered particles. The continuous scanning of the AFM tip ‘cleans’ the surface.
3.3.2 Chemical composition analysis

The chemical composition of the sample was analyzed with the EDX in ESEM, operated in low vacuum. Fig. 3.10 shows the same area of sample as shown in Fig. 3.8. Position ‘a’ is the flat area and position ‘b’ is the rough area nearby. The EDX spectra show:

a) there is trace amount of Si signal, indicating very low concentration of Si in the sample;
b) the Si signal intensity in the flat area is lower than that in the rough area nearby;
c) A black spot was found in the position where EDX analysis was carried out. The high energy e-beam bombarded the surface and evaporated the materials;
d) The surrounding area seemed to be cleaned by the e-beam. This was demonstrated more clearly in Fig. 3.11. EDX analysis was continuously carried out at the same spot. And the spectra at different time intervals were recorded. The spectra show the Si signal decreases insignificantly with the analysis time. After 140 seconds of e-beam radiation, the intensity of the Si signal decreased to the background level. This
experiment shows the layer containing Si signal is very thin, which can be evaporated by the bombardment of the e-beam.

The EDX analysis of the samples in the 3 different Ca(OH)$_2$ solutions show similar results (Fig. 3.12). The Si signal intensity (10-20 counts/second) is much smaller than the Ca signal (400-500 counts/second). In all the samples, no Na signal was detected, while in the previous experiment (section 3.2, Na was found in the sample rinsed with alcohol) (Fig. 3.13).

Fig. 3.10 ESEM and EDX analysis of the reaction product on the calcite substrate: Position a is the flat area in Fig.3. Position b is the rough area nearby.

Fig. 3.11 ESEM images before (up left) and after (up right) the EDX analysis. Continuous EDX analysis at the same spot.
Fig. 3.12 Signal intensity of Si and Ca in the EDX spectra of the reaction product.

Fig. 3.13 ESEM images and EDX spectra of the reaction products on calcite substrate. ESEM images: samples without (left) and with (right) storing in Ca(OH)$_2$ solutions for one month. EDX spectra: sample was stored in Ca(OH)$_2$ solution (solid line); samples were not stored in Ca(OH)$_2$ solution and were rinsed with water (dash line) or alcohol (dot line).
3.4 Samples from University of Bourgogne, Dijon, France

The experiments didn’t succeed in reproducing the atomically flat C-S-H as presented in the literatures[20, 21, 69, 70, 86]. The reasons remained unclear after discussions with the authors, Dr. Lesniewska and coworkers at University of Bourgogne, Dijon, France. The authors sent us some of their samples with atomically flat surfaces, which were previously imaged with contact mode AFM in liquid in their lab by C. Plassard. And the results were confirmed to be the same as those in their publications, as shown in Fig. 3.14. The samples were stored in Ca(OH)₂ solutions.

In our lab, the samples were removed from the solution and dried to be studied with AFM under N₂ atmosphere, following the instructions of the authors, i.e. the samples were rinsed stepwise with alcohol of 3 concentrations (first 50%, then 60% and finally 70%) and dried with N₂ flush. The dried samples were investigated with AFM, ESEM, and EDX.

![Figure 3.14](image)

Fig. 3.14 The samples from University of Bourgogne, Dijon, France, were imaged with contact mode AFM in liquid by C. Plassard before the samples were presented to our lab.

3.4.1 Topography studied with AFM and ESEM

The dried samples were imaged first with contact mode AFM under N₂ atmosphere, then with ESEM in low vacuum conditions (1 mbar of water vapour). The topography show some micro-domains with reasonable flat areas (Fig. 3.15), resembling the surface structures as tested by C. Plassard at University of Bourgogne (Fig. 3.14). However, the surfaces in Fig. 3.15 were not as smooth as those in Fig. 3.14. The difference could be due to the drying process when they were removed from the Ca(OH)₂ solution.
On the surface some big particles with cubic shapes were also observed both in AFM images and in ESEM images. The particles are around several µm high and could not be easily imaged with AFM since the height is out of the AFM scanning range in z direction. The convolution of AFM tip and particles edges gives the pyramid-like structure, which is actually the side-wall of the tip.

3.4.2 Chemical composition analysis with ESEM-EDX

After the AFM studies of the topography of the samples from University of Bourgogne, the surface chemical compositions were analyzed with ESEM-EDX in low vacuum conditions (1 mbar of water vapor). The EDX analysis on the flat area shows the chemical compositions to be C, O and Ca. No signal of Si is detected above the background signal (Fig. 3.16). The EDX spectrum of the homemade sample (Fig. 3.13) is also plotted together for comparison. Both spectra show signal of C, O and Ca. However, the homemade sample shows a trace amount of Si, while the sample from University of Bourgogne shows no trace of Si (more clearly shown in the inset spectrum). Previous chemical composition analysis experiments (section 3.2) show that the very small signal of Si compared to the big one of Ca corresponds to about a 20 nm layer in the bowl of about 1 µm the EDX encompasses. EDX can detect very thin layer
and show signal intensity bigger than the background signal. The results indicate no C-S-H in
the samples from University of Bourgogne.

3.5 Surface polishing with FIB milling

FIB was used to polish the reaction product of calcite crystal and water glass solution. The
polished sample shows a smooth surface with a roughness of about 0.19 nm (RMS) over the
scan size of 700x700 nm (Fig. 3.17c).

The polished surface was studied by AM-SPFM+KPM with RH ranging from 9% to 60%. No
indication of water condensation is observed (Fig. 3.18).

The adhesion force between the AFM tip (Si₃N₄) and surface is measured with AFM as a
function of RH (7% to 80% to 7%). On the FIB polished surface, the adhesion force stays
constant (at around 5 nN). On freshly-cleaved mica, the adhesion force increases from 4 nN to
8 nN at 20-30% RH, and levels off when RH increases to 85%. This change is reversible
when the RH decreases (Fig. 3.19). The standard deviation shows that the measurements are
rather precise, with the deviation of 0.1-0.3nN, (around 5% of the average value).

The adhesion force measurements show that the mica surface is hydrophilic and the FIB-
polished calcite is hydrophobic. The surface of calcite is possibly modified by the Ga ions.
Fig. 3.17 FIB polished sample. a) SEM image; b) and c) AFM topography images.

Fig. 3.18 Topography of FIB-polished surface under increasing RH studied with AFM operated in AM-SPFM+KPM mode.

Fig. 3.19 Adhesion force as functions of RH: average (left) and standard deviations (right).
3.6 Single tobermorite crystal from Autoclaved Aerated Concrete (AAC)

3.6.1 Microstructure and composition analysis of the AAC sample

Examined with the ESEM, the microstructure of freshly-fractured surface of AAC can be classified into three types of components, as shown in the Table 3.1. X-ray diffraction (XRD) spectrum clearly showed crystalline quartz and tobermorite as main composition.

Table 3.1 The microstructure and composition of AAC sample

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>Quartz, SiO₂</td>
</tr>
<tr>
<td>T</td>
<td>Tobermorite</td>
</tr>
</tbody>
</table>

The XRD spectrum of AAC powder shows peaks corresponding to quartz and tobermorite. The microstructure of the AAC sample can be categorized as follows:

1. Flat and dense: quartz (SiO₂)
2. Micro-crystallites: C-S-H, tobermorite
3. Amorphous phase: composed of Ca, Si, Al, K

3.6.2 Nano-manipulator

By using the ESEM equipped with the Nano-manipulator, a single tobermorite was separated from the AAC and put on a Si substrate (Fig. 3.20). It is often moved away by the scanning tip and cannot be found under AFM. The cloud-like scratches are the traces of the movement of the sample (from up to down direction) (Fig. 3.20e).
Chapter 3

The thermoplastic (Tempfix™ mounting adhesive) was proved to be good for fixing the micro-crystal. The specimen is not moved away by the scanning tip even when bigger forces are applied between the tip and the sample (Fig. 3.20f).

![Fig. 3.20](image)

**Fig. 3.20** a) Nano-manipulator approached to the selection location; b-c) crystals were separated from AAC and put on Si substrate; d) Relocation under AFM; e) AFM tip moved sample around; f) Tempfix adhesive fixes the specimen on substrate.

### 3.6.3 Nano-structure of the tobermorite

On the crystal surface, the nano-structure can be obtained with higher resolution by scanning in the smaller area (Fig. 3.21a). The crystal is made up of bundles of finer structure with step of 3nm, which is approximately 2 layers of 1.4-tobermorite. The EDX-analysis also shows the chemical composition to consist of O, Si and Ca, indicating the sample to be crystalline form of C-S-H, tobermorite.

To better compare the surface structure details at different RH, AFM images are acquired by scanning along the fiber direction and then processed by flattening with software (1st order flatten line by line), as shown in Fig. 3.21 b-e). In the scanning area of 500x500nm along the fiber direction at the area as marked in Fig. 3.21a), the image z range is around 15nm. After flattening, the image z-range is around 6 nm. The nanostructure can be better resolved.
3.7 Discussion

3.7.1 The surface structure of the synthesized C-S-H

Two methods were tried to reproduce the atomically smooth C-S-H surface by the same chemical reactions between calcite crystals and water glass solutions. In the first method, the samples were not stored in the \( \text{Ca(OH)}_2 \) solutions (Sample A and B). In the second method, however, the samples were stored in for \( \text{Ca(OH)}_2 \) (Sample C) solutions one month. The reactions were stopped by rinsing with water (Sample A) or alcohol (Sample B, C and D) and the surfaces were dried with \( \text{N}_2 \). The different sample preparation conditions are summarized in Table 3.2. Sample A, B and C are homemade samples and Sample D is the sample from Dr. Lesniewska and coworkers at University of Bourgogne, Dijon, France.
### Table 3.2 Samples prepared under different conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stored in Ca(OH)$_2$ solutions</th>
<th>Rinsed with water</th>
<th>Rinsed with alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Sample B</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Sample C</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Sample D</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Topography and chemical composition analysis of the samples prepared under different conditions show the following results:

1. Surface morphology: All the homemade samples (Sample A, B and C) show similar surface structure, i.e., the reaction product forms a thin layer on the calcite substrate, bearing a cauliflower-like structure. Sample A and C show homogeneous surface structure, while sample B shows varied morphology. Sample D (from University of Bourgogne) shows reasonably flat surfaces;

2. Chemical compositions: The signal intensity of Si is very small, compared to the Ca signal. Sample A and B showed same level of Si concentration without Na signal, while sample C show higher Si intensity with much Na. Sample D show no trace of Si signal at all.

The preparation process by storing the samples in the C-S-H pre-saturated Ca(OH)$_2$ solutions didn’t change the nature of the reaction products. Some parts of the thin layers are poorly adhered to the calcite substrate and can be removed by the scanning AFM tip in contact mode, which exposed the atomically flat micro-domains of calcite substrate. The micro-domains are developed in the dissolution process of calcite. The nano-spherules coverage is from the deposition of the C-S-H. No atomically smooth micro-domains were reproduced as described in the literature[20, 21, 69, 70, 86]. The reason remains unclear. It seems that the thin layer of C-S-H precipitation didn’t undergo the partially re-crystallization process in the Ca(OH)$_2$ solutions, which is the key mechanism in their interpretation[20, 21, 69, 70, 86]. In their publications, the chemical compositions of the atomically smooth micro-domains were not given. Is it essentially C-S-H? Our ESEM-EDX analysis on some of their samples shows no trace of Si and the flat micro-domains are composed of C, O and Ca. The results suggest the atomically flat surface to be possibly CaCO$_3$. 

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3.7.2 Artefacts of FIB milling technique

In FIB milling process, the Ga ions are accelerated toward the target sample and the highly energetic ion beam interacts with the materials, producing artifacts[87-89]. Some examples are present in our experiments:

1. Ion implantation: detection of the implanted Ga ions in TEM-EDX spectrum (Fig. 3.5d);
2. Modification of the surface structure and properties: The FIB-polished calcite show an amorphous surface (Fig. 3.17c). The results of AM-SPFM+KPM and adhesion force as functions of RH are not the same as the results on the natural calcite surface;
3. Artificial structures from FIB polishing: grooves with depth variation of about 0.5nm on FIB milled Ca₃SiO₅ particle surface (Fig. 3.22, roughness (RMS) is about 0.16nm over area of 1x1 μm). With better controlled conditions and operation skill of the FIB, it can be diminished, as shown in Fig. 3.17c;

![AFM topography image of FIB polished Ca₃SiO₅ particle.](image)

Fig. 3.22 AFM topography image of FIB polished Ca₃SiO₅ particle.
Chapter 4 AFM studies on single tobermorite crystals from AAC

Single tobermorite crystals from AAC are studied with Atomic Force Microscopy (AFM) under a controlled climate. The results are compared with the AFM studies on mica.

4.1 Wetting phenomena of mica surface studied by AFM

The studies of the water molecular films on mica surface are important because:

- Mica is a model material (atomically flat surface, well-known properties);
- The results can be used as indications to test and evaluate the instrumentation;
- Mica and cementitious materials have high similarity in both crystal structure and chemical compositions.

The water molecular films on mica were studied with AM-SPFM+KPM (its principle is presented in Appendix I). The RH was decrease from the ambient condition (45%) to 10%. The main results (Fig. 4.1) are:

1. At about RH 45%, some islands were found on the mica surface;
2. When RH decreased, some holes were formed inside the islands and at last the island disappeared and no contrast was detected at RH 36%.
3. At 26.3%, some small features appeared and at 22.6% channels were formed. The profile shows the layer thickness to be twice of diameter of water molecule (0.6nm);
4. Such feature maintained even when the RH was decreased to 10%. In a larger scan area, some pan-cake like films were found in the scan area, which is formed by the tip-surface contact and capillary condensation or contamination, as discussed by Xu et al.[90, 91].

This experiment shows AM-SPFM+KPM to be able to detect water layers on the smooth mica surface. The long range polarization force overcomes the problem of mechanical contact.
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4.2 Surface structure of tobermorite as a function of relative humidity

Fig. 4.2 shows the topography obtained by Tapping mode AFM in the wetting process (RH increases from 7-8% to 81%). The images in the upper column are the 2-D images after flattening. The images in the lower column are the corresponding 3-D images before flattening. No obvious structure changes are observed, except some particle-like structures appear in the scanning area. These structures (around 100nm in size and 3nm in height) are speculated to be contamination. No indication of moisture condensation is observed. This is further confirmed by AM-SPFM+KPM mode (Fig. 4.3). The resolution of surface structure is lower in the XY plane due to the increased tip-surface separation (> 10 nm), while it remains in the angstrom level in the z-direction.

Fig. 4.1 Drying process of the water films on mica, observed by the AM-SPFM+KPM.
4.3 Adhesion force as a function of relative humidity on tobermorite

The adhesion force keeps constant in the whole wetting and drying processes (RH ranges from 7% to 80%, back to 7%). The standard deviation is 0.2-0.3nN, (<5% of the average value) (Fig. 4.4). The topography of the sample surface does not change in the wetting and drying cycle, as shown in Fig. 4.5.

The result of the adhesion force measurements indicates the tip-tobermorite system to be hydrophobic. A comparison experiment of the same tip on hydrophilic mica surface shows that the AFM tip to be hydrophilic. The tobermorite surface is thus hydrophobic.
4.4 Rehydroxilation treatment of the tobermorite surface

The tobermorite surface could be changed by the electron beam in the sampling process with nano-manipulator in ESEM. To re-hydroxylate the surface, the hydrothermal treatment is carried out in saturated water vapour at 85°C for 1.5 hours. This is operated under N₂ atmosphere to avoid the carbonation of the surface. Fig. 4.6 shows the adhesion force on the hydrothermal treated surface as a function of relative humidity. The adhesion force keeps unchanged when the RH increases from 7% to 80%.

As a contrast experiment, the same AFM tip is used to measure the adhesion force as a function of RH on freshly-cleaved mica surface. The adhesion force changes from 5 nN to 9 nN at around 30% RH. This indicates that the AFM tip is hydrophilic.

![Graph showing adhesion force as a function of RH](image)

**Fig. 4.4** Adhesion force between the AFM tip and tobermorite as a function of RH: average value (left) and standard deviation of the 1024 values at each RH (right).

![Image showing tobermorite surface before and after wetting and drying process](image)

**Fig. 4.5** Tobermorite surface before and after the wetting and drying process.

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4.5 Discussions

The interpretation of the adhesion force measurements depends on the experimental system. When the surface is an ideal sample like the atomically flat mica surface, it is straightforward to interpret the results. Only when the surfaces of both tip and sample are hydrophilic, the functions show the form of Type A or B (Table 4.1). When the sample surface is rough, the correct interpretation must, however, consider the roughness of tip and sample.

4.5.1 Adhesion force as a function of RH on mica

Depending on the experimental systems, there are four types of curves of the adhesion force changing with relative humidity (RH). The scheme is shown in Table 4.1. At low RH, the water film on the surfaces are too thin to form the capillary. The forces are mainly van der Waals forces. As the RH increases, the water vapour condenses around the defined space between tip and surface to form an annulus, and thus capillary force and surface tension force contribute to a steep increase in the medium RH of region II. Thus the adhesion force measurement as a function of RH can be used as an indication of the hydrophilicity of the sample surface.
### Table 4.1 Different types of the adhesion force curves as a function of RH

<table>
<thead>
<tr>
<th>Types of function</th>
<th>Description</th>
<th>References</th>
</tr>
</thead>
</table>
| Type A | At medium RH (region II) the adhesion forces increase sharply to double the force at low RH (region I). After the increase, the forces reach a peak value and decrease gradually as RH increases further (region III). | • Both tip and sample surfaces are hydrophilic;  
• These changes are reversible when RH decreases;  
• type A[90, 92-96];  
• type B[94, 97-101] |
| Type B | Region I and region II are the same as in type A. In region III, the force level off or slightly increase to high RH. | Either the tip or the sample surface is hydrophobic [92, 93, 96, 100, 102-104]. |
| Type C | The adhesion forces do not change with the RH; | • Micro-sphere against flat surface [96, 104-106];  
• Water film adsorption amount on mica[107, 108];  
• Between particles[105, 106] |
| Type D | The forces remain small at low and medium RH (up to as high as 80%-90%), only in close to saturate conditions >90%, then increase rapidly. | |

#### 4.5.2 Influence of AFM tip’s radius and geometry

The radius of the very end of the AFM tip can largely vary the adhesion forces. In the model of sphere-plane, the van der Waals force is related to the radius $R$ by $F_{vdW} = \frac{A R}{D^2}$, and the capillary force is related by a simplified calculation $F_c = 4 \pi \gamma R \cos \theta$ (refer to the Appendix). In the case of AFM—mica, because of the small size of the tip (comparable to the capillary-condensed annulus), the adhesion force as a function of RH also shows remarkable dependence on the geometry of the tip [92, 109, 110].

#### 4.5.3 Influence of sample’s roughness: nano-contact asperity

The influence of the surface roughness on the adhesion force as a function of RH can be described in 3 cases (Table 4.2)[101, 111]. In our experiments, the adhesion force
measurements show: In small surface corrugation (sizes of steps or grooves much smaller compared to the AFM tip size), surface roughness seemed not to play an important role in the measurement distribution. When the sizes of corrugation (steps or grooves) were comparable to the size of AFM tip, the force measurement distribution was broaden (Fig. 4.7 and Fig. 4.8). The results are summarized in Table 4.3.

Table 4.2 Multiple asperity contacts between the sphere and substrate[96, 101, 112-117]

<table>
<thead>
<tr>
<th>Cases</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H and $r_p$ are height and radius of the asperity peak, r is radius of the meniscus</td>
<td></td>
</tr>
<tr>
<td>$2r &lt; H$</td>
<td>Asperity regime ($2r &lt; H$): The meniscus is formed between the asperity and the sphere. The capillary force is dominated by the accumulation of fluid around a single asperity and can be calculated by: $F_{ad} = 2\pi r_p (\cos \theta_1 + \cos \theta_2)$</td>
</tr>
<tr>
<td>$2r \sim H$</td>
<td>Roughness regime ($2r \sim H$): The meniscus is formed around a small number of asperities and the condensed liquid occupies a statistically rough region. The adhesion force is determined by the number of asperity contacts (N), and can be calculated by, $F_{ad} = N \cdot 2\pi r_p (\cos \theta_1 + \cos \theta_2)$</td>
</tr>
<tr>
<td>$2r &gt; H$</td>
<td>Sphere regime ($2r &gt; H$): The meniscus is formed between the surface and the sphere. The wetting region is determined by the curvature of the sphere (R). The asperity peak increases the separation distance and the area of the condensed vapour phase. The adhesion force can be calculated by: $F_{ad} = 4\pi R \left[ (1 - H) / 2r \right]$</td>
</tr>
</tbody>
</table>

Fig. 4.7. The distribution of the adhesion force measurements on mica and tobermorite crystals with different topography, data from Fig. 4.4 and Fig. 4.6.
Table 4.3 Summary of the results in Fig. 4.7 and Fig. 4.8

In Fig. 4.7, the surface roughness influence the force measurements in distribution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adhesion force (nN)</th>
<th>Roughness</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Standard deviation</td>
<td>RMS (nm)</td>
<td>Area (nm²)</td>
</tr>
<tr>
<td>mica</td>
<td>4.70</td>
<td>0.14</td>
<td>0.03</td>
<td>600x600</td>
</tr>
<tr>
<td>Tobermorite</td>
<td>4.39</td>
<td>0.16</td>
<td>2.60</td>
<td>600x600</td>
</tr>
<tr>
<td>Tobermorite 2</td>
<td>4.54</td>
<td>0.38</td>
<td>4.72</td>
<td>800x800</td>
</tr>
</tbody>
</table>

In Fig. 4.8, the surface roughness influences the force measurements in magnitude. The AFM tip size: around 20-40nm diameter and the angle of the side wall is around 35°. The size of the groove: 50nm wide (y direction) and around 10nm deep (z direction)

<table>
<thead>
<tr>
<th>Positions</th>
<th>Adhesion force</th>
<th>Situation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position 1</td>
<td>4.95 nN</td>
<td>bottom of the groove, multiple tip-groove contacts.</td>
</tr>
<tr>
<td>Position 2</td>
<td>3.79 nN</td>
<td>protruding edge of the groove, contact area is reduced,</td>
</tr>
<tr>
<td>Position 3</td>
<td>4.43 nN</td>
<td>flatter area; contact area lies between position 1 and 2</td>
</tr>
</tbody>
</table>
4.5.4 Rehydroxylation

The hydrophilicity of the surface can be changed by modifying the surface chemistry in the sample preparation process. For example, when quartz was preheated above 300°C, its hydrophilic surface silanol groups —Si(OH)—Si(OH)— gave off water, leaving behind hydrophobic surface silanol groups —Si—O—Si—, and the contact angle rose from 0 to about 60° (page 320 in[111]). On the other hand, when the rehydroxylation of amorphous silica particles were produced by hydrothermal treatments[106], the silanol density increased, and so did the adhesion force between particles.

In our experiments, the process of separating the single crystal from the AAC is carried out in the ESEM using the nano-manipulator. The continuous imaging of the ESEM on the sample results in the bombardment of the sample surface by the electron beam. The high energy of e-beam bombardment might modify the surface, causing the surface silanol groups to give off water and to become hydrophobic. However, in further experiments of hydrothermal treatment (Fig. 4.6), the hydrophilicity of the tobermorite crystal surface does not change.

4.5.5 The contamination of the thermal plastic—Tempfix Adhesive

Another possible reason of the hydrophobic behaviour of the tobermorite crystal surface (whose native surface was expected to be hydrophilic) is the contamination from the mounting material, thermal plastic. This possibility can be excluded in the contrast experiment of the rehydroxylation (Fig. 4.6). Before measuring the adhesion force volume, the tobermorite crystal was relocated under AFM in contact mode. The tip is scanning (scratching) on the mounting adhesive surface, which is expected to contaminate the AFM tip. But the adhesion force function of the RH shows the tip surface to be hydrophilic (Fig. 4.6) and AFM tip is not contaminated by the thermal plastic.

Both the topography studies and the adhesion force studies suggest that the prepared tobermorite crystals surfaces are hydrophobic. The rehydroxylation process does not change hydrophobicity of the surface. However, on the macroscopic level, AAC is prone to water adsorption in contact with water both liquid state and gas state. The interpretation of the AFM results on tobermorite surface is not so straightforward as the results on mica surface. The artefacts from the separation process can not be completely excluded.
Chapter 5 Discussions and conclusions

The wetting phenomena are studied on the surfaces of three different materials, calcium hydroxide (Ca(OH)₂), mica and tobermorite separated from AAC. The AFM investigation results show the Ca(OH)₂ and mica to be hydrophilic, while tobermorite to be hydrophobic. The abnormal wetting phenomena observed on the tobermorite surface is possibly due to the artifacts induced by the sample preparation process, as discussed in the chapter 4. The surface is unlikely the same as that of natural tobermorite crystal.

5.1 Wetting, hydrophobic interaction and hydrogen bonds

In general, the wettability of the solid surface is determined by its hydrophilicity, which is a complex result of the surface chemical compositions and local atomic charge distributions. The intermolecular interactions between the solvent and the solid surfaces are known as hydrophobic interaction and hydrogen bonds (H bonds)[111].

H bond is predominantly an electrostatic interaction between electronegative atoms and H atoms covalently bound to similar electronegative atoms. Its strength (10-40 kJmol⁻¹) is stronger than the typical van der Waals ‘bond’ (~1 kJmol⁻¹) and much weaker than covalent or ionic bonds (~500 kJmol⁻¹). H bonds play a particularly prominent role in water and the wetting of solid surfaces.

Water molecule can link to other water molecule with 4 H bonds to form tetrahedral network structure, i.e. in ice. In liquid water, the mean number of H bonds per molecule is about 3.5.

When an inert solute molecule contact with water, it disrupts the existing water structure. The water molecules reorient themselves around the solute and form a new and more ordered structure (higher coordination) than in the bulk liquid. It is entropically very unfavourable. The mainly entropic nature of this immiscibility is known as hydrophobic effect. The unusually strong attraction between the hydrophobic molecules or hydrophobic surfaces is described as hydrophobic interaction. When water comes into contact with hydrophobic surfaces, it rolls up into small lenses and subtends a large contact angle on them.

On the contrary, hydrophilic molecules and groups are water soluble and repel each other strongly in water. The solvent-surface interactions strongly resemble solvent-solvent behavior. For example, the relative polarity of the silanol group compared to the –OH in water is important to the hydrophilicity of the solid surface [118]. Surface chemistry has greatly
different substrate-specific effects on the structure and dynamics of interfacial water, i.e, H-bonds number and nearest neighbor coordination number[119, 120].

Hydrophilic surfaces are wetted by water. When two hydrophilic surfaces are brought close to each other, capillary condensation will occur in the confined space in between and the capillary forces exert on them, as discussed in the appendix.

5.2 The wetting of mica, Ca(OH)$_2$ and tobermorite

The three minerals all bear layer structures and all show good cleavage along the (001). The cleaved surfaces are hydrophilic in natural states from the point of view of their surface chemistry. Table 5.1 summarizes their crystal structure features and the properties of adsorbed water on the surface.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Lime</th>
<th>Tobermorite</th>
<th>Muscovite mica</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca(OH)$_2$</td>
<td>Ca$_4$(Si$_3$O$_9$H)$_2$Ca·8H$_2$O</td>
<td>KAl$_2$(Al,Si)$<em>3$O$</em>{10}$(OH)$_2$</td>
</tr>
<tr>
<td>Layer structure</td>
<td>Central Layer</td>
<td>Octahedral Ca-layer; Tetrahedral OH-layer;</td>
<td>Octahedral Ca-layer; Tetrahedral Si-layer</td>
</tr>
<tr>
<td></td>
<td>Interlayer</td>
<td>H-bonding</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>Cleaved surface</td>
<td>Ca$^{2+}$ and OH$^-$</td>
<td>Silanols and possibly Ca$^{2+}$</td>
<td>Silanols, aluminol, and K$^+$</td>
</tr>
<tr>
<td>Structure of the adsorbed water layer on the surface</td>
<td>The ability of the water molecules to both donate and accept H-bond create a well developed H-bonding network across the interface structurally resembling that of bulk liquid water[121]; Non-bridging oxygens (Si-O') and Si-OH groups provide a structure on which water molecules are organized to build an effective H-bonding network [122, 123]; A single interface layer composed of two layers: 1) the adsorbed layer, water molecules are adsorbed on the ditrigonal cavities, at 0.13nm above relaxed surface O plane formed by the 6 SiO$_4$-tetrahedra; 2) the first hydration layer located at 0.25nm above the O-plane[121]</td>
<td>No data for tobermorite, but for kanemites*; Non-bridging oxygens (Si-O') and Si-OH groups provide a structure on which water molecules are organized to build an effective H-bonding network [122, 123]; A single interface layer composed of two layers: 1) the adsorbed layer, water molecules are adsorbed on the ditrigonal cavities, at 0.13nm above relaxed surface O plane formed by the 6 SiO$_4$-tetrahedra; 2) the first hydration layer located at 0.25nm above the O-plane[121]</td>
<td>* Kanemites = [(Na,K)HSi$_2$O$_5$·nH$_2$O]</td>
</tr>
</tbody>
</table>

Muscovite mica has a layered structure of aluminum silicate sheets weakly bonded together by layers of potassium ions. The aluminum silicate sheets is composed of the tetrahedral (Al,
Si)O₄ chains (arranged in ditrigonal rings, 25% occupied by Al and 75% by Si) and octahedral Al layer. The potassium ions occupy large holes between 12 oxygen atoms, 6 from the layer above and 6 from the layer below; the resulting K-O ionic bonds are rather weak and easily broken. [124-127]. (see Fig. 5.1)

![Diagram of muscovite mica (001) surface](image)

**Fig. 5.1** The muscovite mica (001) surface, composed of the basal oxygens of the top SiO₄ tetrahedra arranged in ditrigonal ring units. From Cheng[124].

For the tobermorite, no data in the literature was found for the structure and dynamics of water molecular in the adsorbed interfacial layer. The real crystal structure of tobermorite is not yet completely solved and is under debate. Models were proposed to fit the experimental data by arranging the central layers and the interlayer in one way or the other. In Hamid’s model, all of the oxygen atoms involved in the dangling bonds of the silicate chain are protonated as hydroxyl groups, so that the structure is neutral. No chemical bonds exist between adjacent lamellae. The interlayer is occupied by water molecules. On the contrary, in Merlino’s structure, the lamellae are linked by bridging Si-O-Si bonds, generating cavities analogous to those found in Zeolites.

In any case, the cleavage surface of tobermorite in (001) will be composed of seven-fold coordinated Ca-octahedra and Si-tetrahedra. The seven-fold coordination of Ca is shown in Fig. 5.3 and Fig. 5.2 [43]. It has a tetragonal pyramid as the top part and a dome as the bottom part. The pyramid top shows positional disorder and is either occupied by water or oxygen. For the Si-tetrahedral in silicate anion chain as shown in Fig. 1.4 [26], all the O atoms in the paired tetrahedral are shared with other tetrahedral forming the Si-O-Si bonds. Some O atoms of the bridging tetrahedral are, however, not in the Si-O-Si bonds and present as silanol...
groups (Si-OH) or non-bridging oxygens (Si-O'). Both Ca-octohedra and the paired Si-tetrahedral serve as H-bonding acceptor or donor. Water molecules are adsorbed onto the surface and form the H-bonding network in the interfacial layer. The surface is hydrophilic.

Fig. 5.3 The seven-fold co-ordination of Ca. the top pyramidal shows positional disorder and is either occupied by water or oxygen (fig.3), from Hoffmann [43]

Fig. 5.2 Connection of silicate chain to the layer of calcium polyhedral, view alone [001], view from [100] in Fig. 1.3, from Merlino [26].
5.3 Tobermorite and C-S-H

The surface chemistry and crystal structure of C-S-H is akin to that of minerals tobermorite or jennite. Tobermorite is used as a model material to simulate the surface properties of C-S-H in the studies where long-range order crystal structure is needed. In the cement paste, C-S-H has a complex structure and composition without long-range order. High-resolution TEM studies show local crystalline C-S-H in several nm range[11]. Thus C-S-H has much shorter Si-anion chain (dreierkette) and more side groups of Si-O and Si-OH than tobermorite crystal. The increased number of silanol group will enhance the surface wettability and hydrophilicity. The various chemical composition and crystal structure result in the complicated morphology and surface properties. The wetting properties on the molecular level might not necessarily the same as that on tobermorite or kanemites, especially the structure and dynamics of water molecular in the adsorbed interfacial layer. Nevertheless, the hydrophilic nature of the surface is the same in the point of view of surface chemistry.

The preparation conditions (heat or high energy e-beam bombardment) may cause the surface silanol groups to give off water and form -Si-O-Si- bridge bonding. The surface has no H-bond acceptor or donator for the water molecules to wet the surface. And the surface becomes hydrophobic.

Other possible reason for the non-wetting is that, in the moist atmosphere, water vapour might enter the interlayer space of tobermorite, instead of accumulating on the surface to form the water films and capillary meniscus. This hypothesis is unlikely since the wetting experiments were carried out in the time span of 30 hours, while in molecular dynamics simulation, the time to reach the thermodynamic equilibrium is 100 ps. Kinetics study[128] of capillary condensation at the nanoscale showed: at 40% RH, the meniscus nucleation time is around 4.2 ms at 299 K. Molecular dynamics study by Kirkpatrick [122, 123] showed that incorporation of large amounts of water in kanemite-like interlayers is energetically unfavorable and, thus, suggest that the interlayer swelling of A-S-H (alkali silicate hydrate) gel is due to incorporation of water molecules between nano-particles, rather than within kanemite-like interlayer galleries.
5.4 Conclusions

5.4.1 Real-time carbonation process of Ca(OH)$_2$ crystal surface

Ca(OH)$_2$ is transformed to CaCO$_3$ only if CO$_2$ and H$_2$O are simultaneously present and the relative humidity (RH) exceeds 30%. The formation of nano-droplets of water is necessary for the gaseous CO$_2$ to react with Ca(OH)$_2$. After a long-term exposure to the ambient air, a spherular layer of CaCO$_3$ is formed.

5.4.2 Synthesized C-S-H

The reaction of calcite (CaCO$_3$) crystal with concentrated solution of water glass (Na$_2$SiO$_3$) produced a thin C-S-H layer (20nm) on the calcite surface. The topography studied by AFM show the surface to be cauliflower-like structure. The micro-domains are originated from the dissolution process of the calcite into the solutions and the nano-spherules are the precipitation of C-S-H from the reaction. No atomically flat C-S-H micro-domains are reproduced as described in the literatures[20, 21, 69, 70, 86].

The samples from University of Bourgogne, Dijion, France, show flat micro-domains with smooth surfaces. The chemical compositions analysis by ESEM-EDX reveals, however, that the surfaces are not C-S-H (no Si signal was detected).

5.4.3 Tobermorite crystals in AAC (Autoclaved Aerated Concrete)

On the surface of the individual tobermorite crystal separated from AAC, both topography studies and adhesion force studies suggest the surfaces to be hydrophobic. The rehydroxylation (under the 85°C in saturate water steam for 1.5 hours) does not change hydrophobicity of the surface. The surface is possibly modified by the electron beam in the sample preparation process.

5.4.4 FIB (Focused Ion Beam)

FIB prepared TEM-lamella (100nm thick) efficiently enhance the EDX analysis resolution (20nm). FIB polishing produces atomically smooth surface (mean roughness RMS of 0.19
nm). The bombardment of the Ga ions produces artefacts, such as Ga ions implantation, re-deposition of milled materials, and modification of surface composition and structure.

5.5 Future work

The experiments have demonstrated some applications of AFM in the cementitious materials, especially on the interaction between moisture and surfaces. The preliminary results indicated the limited application of AFM in cementitious materials is due to sample preparation. Several techniques have been tried to prepare AFM samples for the wetting phenomena studies. The interpretation of the results is not so straightforward to reveal the nature of the surface wetting properties. Further work can be focused on:

1. It remains an open question if the atomically flat surface is C-S-H produced by chemical synthesis via reaction of calcite crystal with water glass. Further experiments are needed to clarify it by investigating the growth rate (layer thickness) and the chemical composition as well as crystal structure of the C-S-H layer coverage on the substrate (calcite) surfaces.

2. In the sample preparation process, the artifacts are produced, for instance, Ga ions implantation in FIB milling, the e-beam bombardment in the ESEM equipped with nano-manipulator. The artifacts should be minimized. For the separation of tobermorite crystal from AAC shall be manipulated without the e-beam effect (not to use SEM).

3. The surface of tobermorite separated from AAC shows hydrophobic phenomenon. The hypothesis is that the silica anion chains dehydrated to form Si-O-Si bonds during the nano-manipulator process. It would be of interest to re-hydrate the surface to produce silanol groups (Si-OH) and the non-bridging oxygens (Si-O), although the thermohydration treatment in this thesis did not succeed in the surface rehydroxilation.

4. The molecular structure of the adsorbed water layer on the surfaces should be studied by combining the AFM imaging technique with other surface analytical methods, such as high resolution specular X-ray reflectivity, nuclear magnetic resonance (NMR). Molecular dynamics simulation of the wetting phenomenon will help to understand the experimental results.
Appendix  AM-SPFM+KPM and force measurements

A.1 AM-SPFM+KPM

Amplitude-modulated Scanning Polarization Force Microscopy with Kelvin Probe Microscopy (AM-SPFM+KPM) [91, 129-141] is used to image water thin films on solid surface under ambient conditions. The critical problem is to avoid the AFM tip-liquid contact. The origin of the polarization force is actually the electrostatic force. This mode combines normal tapping mode and the Kelvin Probe Microscopy and it can simultaneously detect the topography, potential and surface charge distribution, and dielectric constant information.

A.1.1 Electrostatic force

When a bias voltage $V_{\text{tip}} = V_{\text{dc}} + V_{\text{ac}} \cdot \sin(\omega t)$ is applied to the tip, the electrostatic force between the tip and surface may be approximated as:

$$F_E = \frac{1}{2} \frac{\partial C}{\partial z} \cdot (V_{\text{tip}} - \phi)^2 \approx -4\pi \varepsilon_0 \cdot \frac{\varepsilon - 1}{\varepsilon + 1} \cdot f\left(\frac{R}{z}\right) \cdot (V_{\text{tip}} - \phi)^2 = B \cdot (V_{\text{tip}} - \phi)^2;$$

$$B = -4\pi \varepsilon_0 \cdot \frac{\varepsilon - 1}{\varepsilon + 1} \cdot f\left(\frac{R}{z}\right);$$

$$F_{0\omega} = B \cdot \left(\frac{V_{\text{dc}}}{R}\right)^2 + \frac{1}{2} V_{\text{ac}}^2; \quad \Rightarrow \text{dc component;}$$

$$F_{1\omega} = B \cdot 2 \left(\frac{V_{\text{dc}}}{R}\right) \cdot V_{\text{ac}} \cdot \sin(\omega t); \quad \Rightarrow 1\omega \text{ component;}$$

$$F_{2\omega} = -B \cdot \frac{1}{2} V_{\text{ac}}^2 \cdot \cos(2\omega t); \quad \Rightarrow 2\omega \text{ component;}$$

Where $C$ is the effective capacitance between the tip and the sample, $z$ is the tip-sample distance, $R$ is the tip radius, $\phi$ is the local contact potential. The function $f(R/z)$ depends on the geometry of the tip and the sample. In the Sphere-Plane model, $R/z >> 1$, $f(R/z) \approx R/z$; for $R/z << 1$, $f(R/z) \approx (R/z)^2$. This electrostatic force drives the cantilever to oscillate at the frequency of $1\omega$ and $2\omega$, which can be detected separately with lock-in technique (Fig. A.1)

A.1.2 Topography

In the normal tapping mode, the cantilever is mechanically driven by the tapping piezoelectric actuator to oscillate at a frequency near to its resonant frequency ($\omega_0$). The main feedback
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loop of the NanoScope IV electronics controller keeps this oscillation amplitude (at $\omega_0$) constant. The feedback signal is recorded to give the topography.

### A.1.3 Surface potential

The amplitude of $1\omega$ component is used as a feedback signal for the second feedback loop to compensate the local contact potential, by adjusting the electrochemical potential between the tip and the sample, i.e. $V_{dc} - \varphi = 0$. This dc output ($V_{dc}$) of the feedback loop is recorded to provide a map of surface charge or surface potential distribution. And because of $V_{dc} - \varphi = 0$, the topography (signal of $\omega_0$) is corrected for the surface charges.

### A.1.4 Surface dielectric constants

The $2\omega$ component provides additional information about the sample’s dielectric constant.

A signal access module (SAM, break-out box, Veeco Instruments, Inc.) was used to provide access to the interface of the data between AFM and electronic controller. The ac bias was generated by a digital function generator (Thurlby Thandar Instruments Ltd. Type TG1010A), with amplitude of 10 V (peak to peak) and the frequency ($\omega$) of 3 kHz (the frequency was chosen to be lower than the mechanical resonant frequency of the cantilever).

![Fig. A.1 Schematic diagram of the principle of the AM-SPFM+KPM](image)
A.2 AFM measurements of adhesion force

A.2.1 Force-distance curves and force volume
An AFM force-distance curve is a plot of the tip-sample interaction forces vs. tip-sample separation distance [34, 35, 142]. A typical force-distance curve is shown in Fig. A.2. Force Volume imaging with AFM combines measured topographic information and the tip-sample interaction forces information into a single data set. At each X-Y position of the selected area, a force-distance curve measurement is performed. The interval of the X and Y and the range of Z can be set to suitable values, and a three dimensional force curves over the area is recorded. Force-Volume makes it possible to test the correlations between forces and surface features, as shown in chapter 4. This image mode is also known as jumping mode [143].

![Force-distance curve](image)

Fig. A.2 Calculation of adhesion force from the Force-distance curves

A.2.2 Calculation of the adhesion force
In the AFM software, the force volume shows topography, adhesion force mapping, and force-distance curves at the specific position. For the mean value and standard deviation of the adhesion force measurements, the data have to be processed with MS-Excel in the following procedure:

1. Export the afm file to ASCII file with raw units as .txt file;
2. Open the .txt file with MS Excel;
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3. Find the minimum of one curve (row) ‘A’, (Fig. A.2);
4. Locate the column number of this found minimum value;
5. Define the ‘zero-line’ ‘B’ (for example, value at 10th data point after ‘A’);
6. Calculate the difference between the minimum value and the zero line ‘B-A’;
7. Repeat 3-6 for each row;
8. Calculate the average value and standard deviation of the calculated forces.

Raw units are converted to nN by using nm/raw parameters and spring constant.
This can be done with a ‘Macro’ in MS Excel.

The Visual Basic program of the ‘Macro’ to calculate the adhesion force mapping. In the case of the data of a force-volume measurement with, topograph=32x32, Force Volume=32x32, Force curve=128 point/line, open the ASCII file with ‘start import at raw’: 258.

```
Sub Macro1()
' Macro1 Macro
' calculate adhesion force, average, stdev

    Range("A1027").Select
    ActiveCell.FormulaR1C1 = "=MIN(R[-1026])"
    Range("B1027").Select
    ActiveCell.FormulaR1C1 = "=MATCH(RC[-1],R[-1026],0)"
    Range("C1027").Select
    ActiveCell.FormulaR1C1 = "=INDEX(R[-1026],1,RC[-1]+10)"
    Range("D1027").Select
    ActiveCell.FormulaR1C1 = "=RC[-1]-RC[-3]"
    Range("A1027:D1027").Select
    Selection.AutoFill Destination:=Range("A1027:D2050"), Type:=xlFillDefault
    Range("A1027:D2050").Select
    Range("F1027").Select
    ActiveCell.FormulaR1C1 = "=AVERAGE(RC[-2]:R[1023]C[-2])"
    Range("F1028").Select
    ActiveCell.FormulaR1C1 = "=STDEV(R[-1]C[-2]:R[1022]C[-2])"
    Range("F1030").Select
    ActiveCell.FormulaR1C1 = "=R[-2]C/R[-3]C"
    Range("G1030").Select
End Sub
```
A.2.3 Spring constant of the AFM probe

The spring constant ($k$) of the cantilever depends on the geometry and materials. In our experiments, the approximate spring constant is referred to the commercial datasheet as well as the quick and easy way as described in the Nanoscope manual [35].

By sweeping the drive frequency, the cantilever is excited to vibrate and the oscillation amplitude is plotted versus the sweeping frequency. The frequency of the peak amplitude is then determined to be the resonant frequency, $f$. With the lock-in technique, the phase lag of the cantilever compared to the driving force can also be obtained. This frequency is then used to calculate the spring constant by the software, depending on the following relation, $k = \alpha \cdot f^3$, where $\alpha$ is some coefficient stored in the NanoScope software.

One example is shown in Fig. A.3. The resonant frequency of the cantilever is 24.32kHz, and the spring constant was calculated to be $k=0.166$ N/m, which is in the range of the values provided by the manufacturer.

![Fig. A.3 Seeking the resonant frequency of the AFM probe.](image)

A.3 Theory of adhesion force

In general, the adhesion force between an AFM tip and a sample surface should include the capillary force ($F_c$) as well as the solid-solid interactions, consisting of van der Waals forces ($F_{vdw}$), electrostatic forces ($F_E$), and the chemical bonding force ($F_B$) [101, 111, 116]

$$F_{ad} = F_c + F_{vdw} + F_E + F_B$$

When the tip and sample are not net charged, $F_E=0$; When the surfaces are saturated with chemical bonds, $F_B=0$. In the following section, $F_c$ and $F_{vdw}$ will be discussed.
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A.3.1 Van der Waals force

For the special case of sphere-plane model, van der Waals force is given by

\[ F = 4\pi R\gamma = \frac{AR}{6D_0^2} \]

\(A\) is the Hamaker constant (\(A = \pi^2 C \rho_1 \rho_2\)), \(\rho_1\) and \(\rho_2\) the number of atoms per unit volume in the two bodies and \(C\) is the coefficient in the atom-atom pair potential \([111]\)). \(D_0\) is the interfacial contact separation. For most solid contacts \(D_0\) can be taken as 2 Å in order to make use of the continuum theory at the atomic scale. The Hamaker constant \(A\) depends on the medium that the two objects are in. For a Si\(_3\)N\(_4\)/SiO\(_2\) contact, if the medium is air, \(A = 10.38 \times 10^{-20}\) J; if the medium is water, \(A = 1.9 \times 10^{-20}\) J \([144]\). Taking \(D = 2\) Å, \(R=10\)nm, we would obtain \(F_{\text{vdW}}(\text{air}) = 4.3\) nN, and \(F_{\text{vdW}}(\text{water}) = 0.8\) nN.

A.3.2 Adhesion force from the annulus of capillary-condensed liquid

Consider a particle or probe (i.e. AFM tip) close to a flat solid wall with a small amount of liquid filling the gap, assuming the problem to be symmetric with respect to the y-axis, thus the capillary surface joining the plate and the particle forms circular contact lines on both of them, as depicted in Fig. A.4. The adhesion force consists of two components:

\[ F_c = F_p + F_s; \]

The term ‘capillary pressure force’ \(F_p\) refers to the force due to the pressure difference across the curved liquid-fluid interface in the capillary space between the tip and the surface. The

Fig. A.4 Geometry of the capillary-condensed liquid between a sphere and a plane.
term “interfacial tension force” $F_s$ implies the force tension acting tangentially to the interface along the contact line with the solid body [109, 110, 145].

$$\Delta p = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right);$$

$$F_p = -\pi r_2^2 \Delta p = -\pi r_2^2 \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$

$$F_s = 2\pi r_2 \sin (\theta + \phi)$$

For a general tip shape $y(x)$ (the contour of the tip cross section),

$$F_p = \pi \gamma x^2 \left( -\frac{1}{x} + \frac{\cos(\theta + \phi) + \cos \theta_2}{D + y(x)} \right)$$

$$F_s = 2\pi \gamma x \sin (\theta + \phi)$$

For a sphere-plane model,

$$F_p = \pi \gamma R \left( -\sin \phi + \frac{\cos(\theta + \phi) + \cos \theta_2}{D/R + 1 - \cos \phi} \right)$$

$$F_s = 2\pi \gamma R \sin \phi \sin (\theta + \phi)$$

where $r_1$ is the radius of the meniscus in a radial cross section ($r_1$ being positive for liquid droplet, negative for bubbles and above capillary held wetting liquids), $r_2$ is the radius of the contact lines, $r_K$ is the mean radius of curvature of the liquid / vapour interface (Kelvin radius), $\theta_1$ and $\theta_2$ are the contact angles of the liquid with the tip and the sample, respectively, $R$ is the radius of the sphere, $D$ is the distance between the sphere and the plane, $d$ is the distance the tip extends into the water bridge, $\phi$ the filling angle of the capillary-condense liquid, $\gamma$ is the liquid/vapor interfacial tension.

Here, the term $D/R$ is very small and is typically ignored for macroscopic spheres [92]. Keeping a finite $D/R$ is in principle important however, since only with it can a vanishing capillary force at zero humidity be obtained. Taking $D=0$ first and then $\phi=0$, the capillary force would reduce to $F_s = 2\pi \gamma R (\cos \theta_1 + \cos \theta_2)$, even at zero humidity.

Assuming that (i) the radii of the solid-liquid contact lines are much smaller than the radius $R$ of the sphere ($r_2<<R$, filling angle $\phi\to 0$), (ii) the radii of the two contact lines are equal ($\theta_1 = \theta_2 = \theta$), (iii) the distance between the sphere surface and the flat surface is very small.
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compared with the radius of the contact line \((D<<R)\), and (iv) the radius of the meniscus in a radial cross section is much smaller than the radius of the contact lines \((r_1<<r_2)\),

1. \(D=0, \phi=0\) (relative humidity RH ~ 0),
   \[ F_c = 2\pi r R (\cos \theta_1 + \cos \theta_2) \]

2. \(\theta_1 = \theta_2 = 0\),
   \[ F_c = 4\pi r R \cos \theta \]

Under the above assumptions, the capillary force is humidity independent. For a Si\(_3\)N\(_4\)/SiO\(_2\) contact, \(R=10\)nm, \(\gamma_{H_2O} = 73\)m J / m\(^2\), \(\theta_{Si3N4} = 60^\circ\), \(\theta_{SiO} = 0^\circ\) [92, 111], the calculated capillary force is \(F_c = 6.9\) nN, which is at the same order as the van der Waals force (4.3 nN).

A.3.3 Adhesion force as a function of RH

To calculate the adhesion force as a function of relative humidity, the filling angle is to be determined by the Kelvin equation.

\[ \left(1 + \frac{1}{r_1/r_2}\right)^{-1} = r_k = \frac{\gamma V}{RT \ln(p/p_s)} \]

Where \(V\) is the molar volume, and \(p_s\) is the saturated vapor pressure of the liquid, \(\gamma\) is the liquid/vapor interfacial tension, \(R\) is the gas constant, and \(T\) is the absolute temperature. This equation predicts a linear relation between \(r_k\) and \(\ln(p/p_s)\).

Thus the relation of filling angle and the relative humidity can be calculated as following:

\[ \frac{\Delta p}{\gamma} = \left(1 + \frac{1}{r_1/r_2}\right) = r_k^{-1} = \frac{RT \ln(p/p_s)}{\gamma V} \]

For a sphere-plan model, it is written as

\[ \frac{RT \ln(p/p_s)}{\gamma V} = \left(1 + \frac{1}{r_1/r_2}\right) = \left(\frac{1}{R \sin \phi} - \frac{\cos (\theta_1 + \phi) + \cos \theta_2}{D + R(1 - \cos \phi)}\right) \]

The thickness of the water film at the contact line can be calculated as

\[ h = D + d = D + R(1 - \cos \phi) \]

These equations were used to fit the AFM studies of adhesion force as a function of RH [92]. However, for dry atmosphere (low RH), Kelvin equation is no more valid for very high curvature systems \((r<3-4\)nm, corresponding to \(p/p_s>0.7-0.8\)) [146-150]. Thus the calculated adhesion force as a function of RH is only valid at RH higher than 70-80%.
References

References


References


References


Curriculum Vitae

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