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Direct observation of the carbonation process on the surface of calcium hydroxide crystals in hardened cement paste using an Atomic Force Microscope

T. YANG, B. KELLER, E. MAGYARI
Chair of Physics of Buildings, Institute of Building Technology, Swiss Federal Institute of Technology (ETH) Zürich, CH-8093 Zürich, Switzerland
E-mail: magyari@hbt.arch.ethz.ch

K. HAMETNER, D. GÜNTHER
Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology (ETH) Zürich, CH-8093 Zürich, Switzerland

The surface carbonation process of calcium hydroxide crystals in samples of hardened Portland cement paste has been investigated at the nanometer scale with the aid of an Atomic Force Microscope (AFM). The AFM, encapsulated in a glove-box, was operated in contact mode at ambient temperature. Successive real-time measurements were performed in (i) a pure non-reacting N_2 atmosphere, (ii) a $N_2 + H_2O$, (iii) a $N_2 + CO_2$ and finally (iv) in a $N_2 + CO_2 + H_2O$ atmosphere, respectively. In the $N_2 + H_2O$ atmosphere, until 30–40% relative humidity, a minor change as surface smoothing with an occurring instability was detected. In the $N_2 + CO_2$ atmosphere, no change was detected, except for some very small grains becoming after two days even a little bit smaller. However, in the $N_2 + CO_2 + H_2O$ atmosphere, i.e., in a simultaneous $CO_2 + H_2O$ environment, with a stepwise increase of the relative humidity until 26%–30%, on the surface of the calcium hydroxide crystals several small scattered spots were found. These spots were weakly linked to the surface and could be pushed away with the scanning tip. Under constant conditions (temperature, humidity- and CO_2-content), the small spots start to grow, and after a long-term exposition of the crystals to the ambient humid air, develop a specific spherular structure. The latter is interpreted to be calcium carbonate, a result of the surface carbonation process of the initial calcium hydroxide crystals. © *2003 Kluwer Academic Publishers*

1. Introduction

Calcium hydroxide, $Ca(OH)_2$, abbreviated usually as CH, is one of the main reaction products resulting from the hydration of Portland cement with water. The fluid cement paste is supersaturated in CH and thus, e.g., by casting of concrete, it precipitates on the smooth surface of the aggregates (gravels) and of the reinforcement steel, giving rise to a thin crystalline layer around them. Consequently, this surrounding CH layer has a major significance for the mechanical properties of the most important building material, the reinforced concrete. Moreover, around the steel bars, due to its alkalinity, the CH layer also forms a protecting chemical screen against the most dangerous damage mechanism of the concrete, the corrosion of its reinforcement. Obviously, the calcium hydroxide is also present in the bulk of the hardened cement paste but its morphology is much different from that of the smooth layer mentioned.

The main danger for the chemical stability of CH in concrete is its "carbonation process," i.e., its reaction in an aqueous environment with the atmospheric carbon dioxide, CO_2, leading to calcium carbonate, $CaCO_3$. As a consequence of the gradual carbonation of CH, the alkaline screen protecting the reinforcement disappears and the corrosion sets on.

Having in mind the above facts, the carbonation process of CH in cementitious materials has attracted an enormous research interest. An excellent selection of this vast topic has been collected recently by Skalny, Gebauer and Odler in [1].

In the previous investigations 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

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the relative humidity (RH) of the atmosphere, which reaches a maximum at intermediate values of RH (50%–70%) [2–8]. 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.

As an alternative, the Atomic Force Microscopy (AFM), [9], is an excellent technique not only because it can provide high resolution topography of microstructure, but also because it combines advantages of digital three-dimensional morphological information in room atmosphere, no vacuum requirements, real-time imaging during reaction [9–11]. In the cement and concrete research, a direct AFM observation was applied to study of the early stage of hydration of calcium silicate hydrate (C-S-H) by Mitchell *et al*. [12] and Gauffinet *et al.* [13]. In the investigation of the growth dynamics of cement gels during hydration, also combined experimental techniques as AFM-SEM [13, 14], AFM-NMR [15], and AFM—single-particle X-ray diffraction [16, 17], were used.

In the study reported in the present paper, reasonably massive flat parts (sizes of hundreds of microns) for AFM investigation from cement paste were prepared by the Mica-Replication-Method (MRM, [18]). The surface layer of these samples have served as a model for the CH layer actually encountered in cementitious materials of the building industry. The chemical composition of the flat area was analysed by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) [19], as well as SEM, back-scattering SEM and EDX-analysis. The AFM investigation of the surfaces was carried out at ambient temperature in a pure non-reacting N_2 atmosphere, $N_2 + H_2O$, $N_2 + CO_2$ and $N_2 + CO_2 + H_2O$ atmospheres respectively. The results provide real-time information of the carbonation process of surface of $Ca(OH)_2$ crystal at nanometer scale.

2. Experimental

The cement paste was prepared in the usual way by mixing the portland cement powder with distilled water with the water/cement ratio of 0.4 (in weight). The mixture was stirred by hand for 5 min, then cast on a freshly-cleaved mica. The samples were wet cured in the presence of an excess of water in a sealed container (100% RH) for 28 days. The pastes were then dried in pure nitrogen (99.995% N_2) and were easily removed from mica due to the stresses produced by the shrinkage of the paste as described by Hadley [20]. The surface of the cement paste was then studied by AFM in a glove-box with N_2, $N_2 + H_2O$, $N_2 + CO_2$ and $N_2 + CO_2 + H_2O$ atmospheres respectively. The relative humidity in the box was controlled by adjusting the ratio of dry N_2 to humid N_2 (N_2 bubbling through a wash flask filled with water), measured by a dew-point hygrometer (Bruel & Kjar, Indoor Climate Analyzer Type1213, humidity transducer MM0037) with an accuracy of the dew point of 1.0°C.

Trace element characterizations of the sample was carried out by the Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). The description of the methods and principles of the measurements on the sample can be found in the literature [19]. In brief, the sample is hosted within an ablation cell on a microscope table, which allows positioning of the sample in X, Y and Z directions. The cell is flushed with an inert gas (usually argon or helium) for scavenging

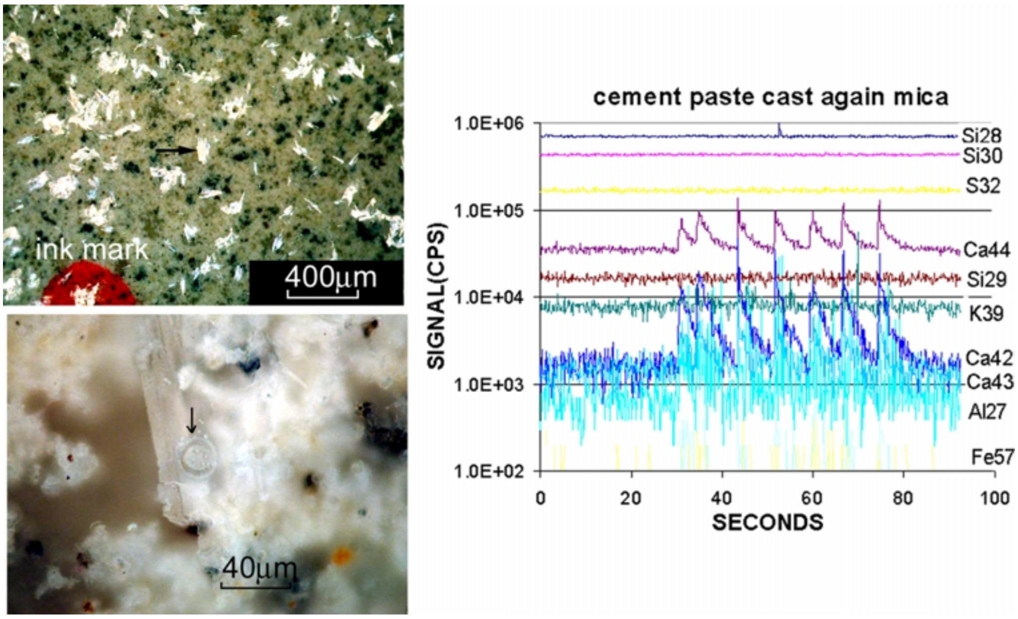


Figure 1 Optical microscope image of the cement paste cast against mica and the signal-time spectrum of the LA-ICP-MS.

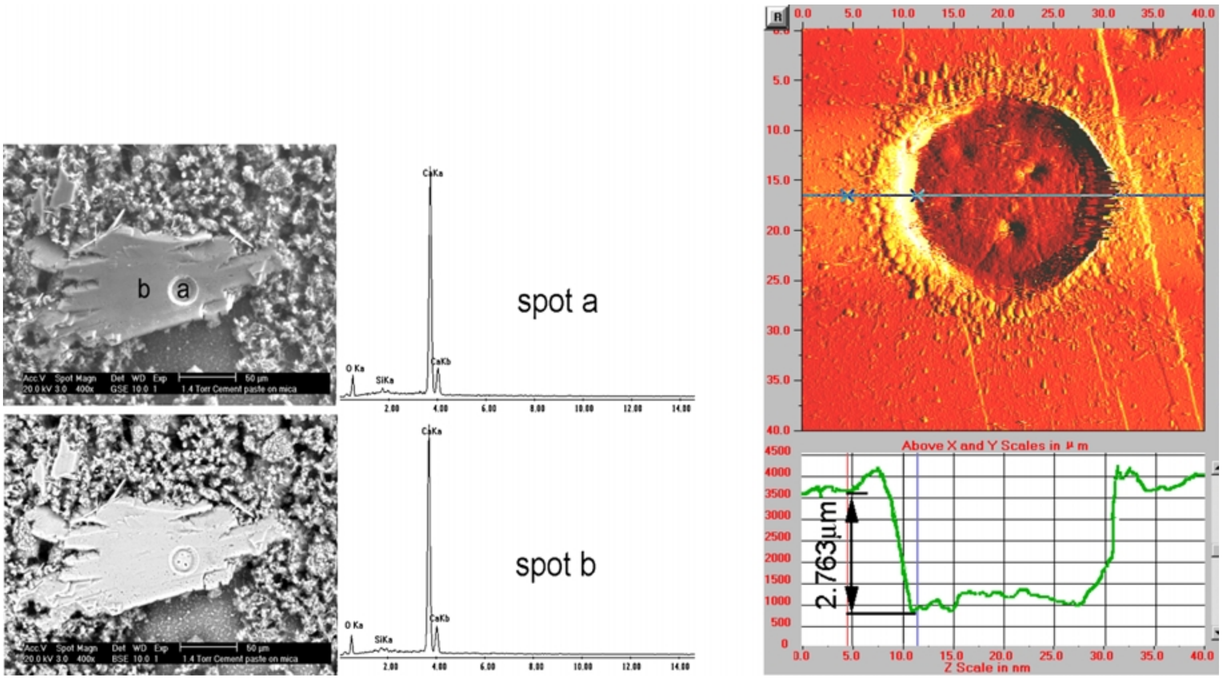


Figure 2 SEM and Back-scattering EM image of area of the laser ablation crater, and the EDX-analyze of the spot a and b. AFM image of the same spot area.

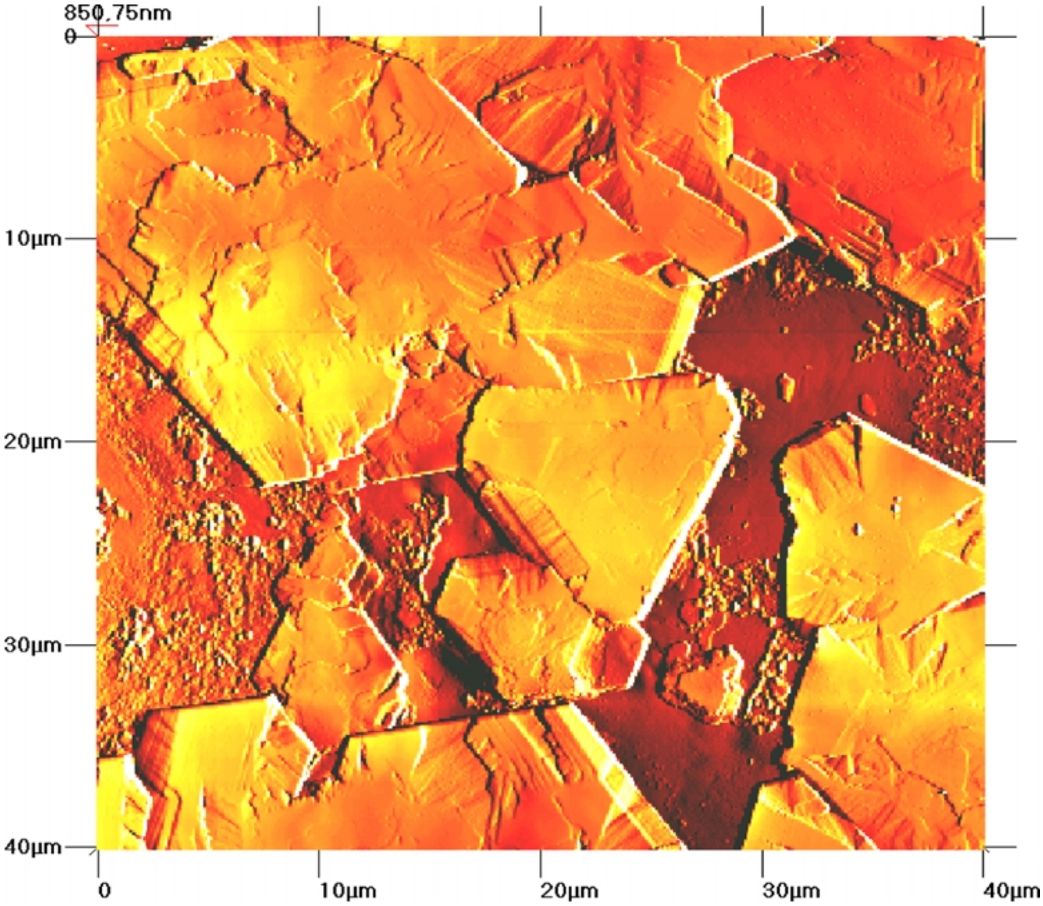
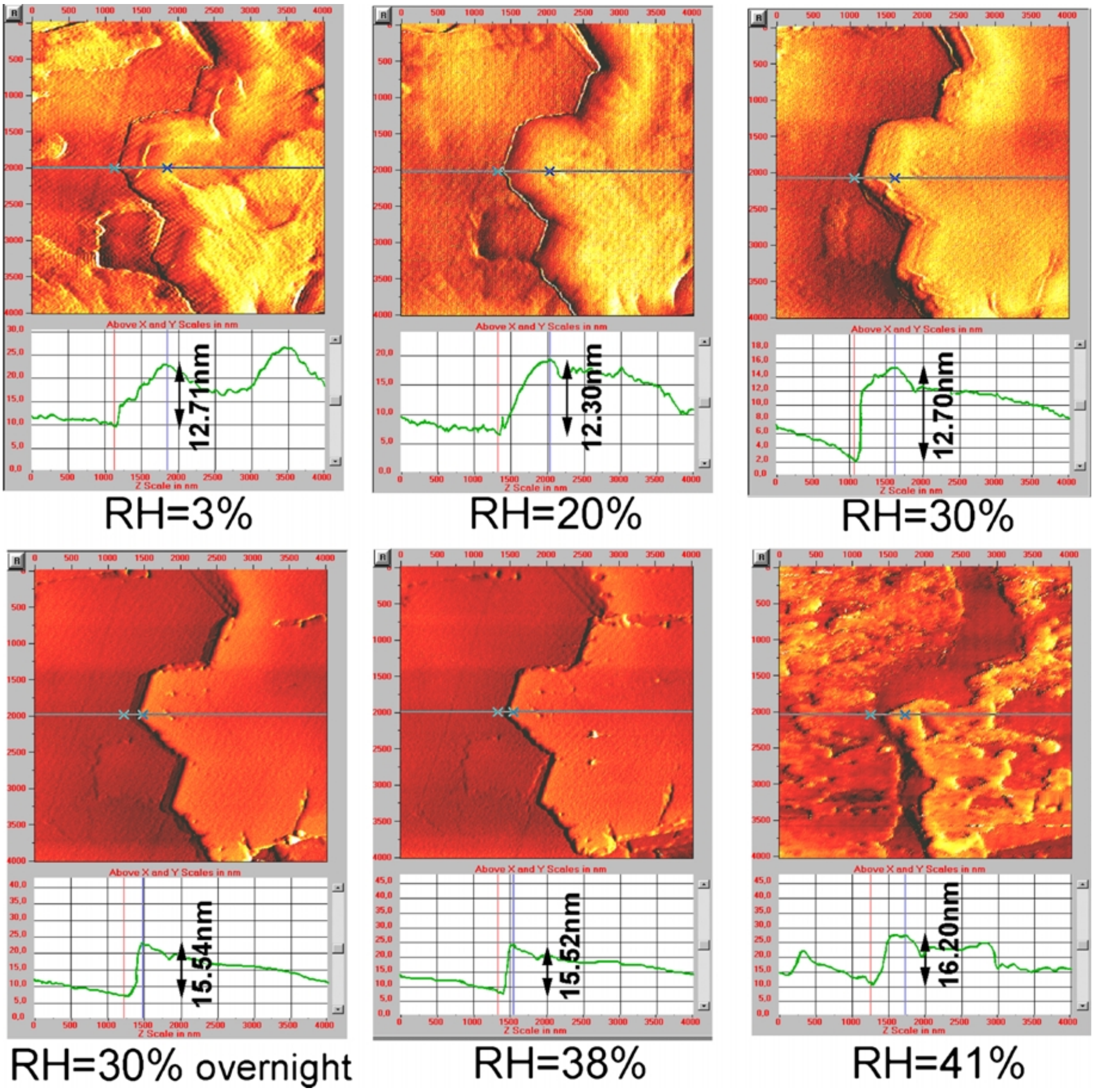


Figure 3 Massive hexagonal crystals on the surface of cement paste.

of the ablated materials. The incident laser beam interacts with the sample surface and the energy converts to ablated material in form of small particles. These released particles from the sample are then transported to an inductively coupled plasma mass spectrometer (ICP-MS), where they get vaporized and ionized for elemental analysis. In this work, the 193 nm ArF excimer laser was used at a pulse repetition rate of 1 Hz and at low energy of 60 mJ (5 J/cm^2) to ensure controlled low sample uptake per pulse. The diameter of the laser spot was 20 microns.

Environmental Scanning Electronic Microscope (ESEM) (Philips ESEM-FEG XL30) was used to investigate the surface structure of the cement pasted. The



RH=3%
RH=20%
RH=30%
RH=30% overnight
RH=38%
RH=41%

Figure 4 Surface structure change with RH in $N_2 + H_2O$ atmosphere.

Energy-Dispersive X-ray (EDX) analysis was applied to identify the composition of the surface.

The AFM (Quesant,Q-250) was operated in contact mode with a 40 μm scanning head; its x–y scan range is 40 μm and its z scan range is 5 μm. Silicon tips used were mounted on a cantilever with a force constant of about 0.2 N/m and the resonant frequency is about 13 kHz. The tip radii are typically smaller than 10 nm. The cone angle is less than 20° at the apex and the height is 10–15 μm.

3. Results and discussion

3.1. Trace element by LA-ICP-MS

Under the optical microscope, one can see the cement paste prepared by MRM to consist of reasonable flat shining areas in hundred μm and some dark pores (Fig. 1). The area was marked with ink under optical microscope and the laser ablation was directed to the spot to release the materials layer by layer and the released materials were transported within a mixture of helium and argon for ionization into the ICP-MS.

The peaks in the transient signal of the LA-ICP-MS spectra (Fig. 1) indicate individual ablations (single pulse) where 13 isotopes were measured. The 7 peaks of the Ca44, Ca 42, Ca43 correspond to the 7 pulses of incident laser beam. No peaks of Si30, S32, A127, K39, Si29, Mg24, Mg25, Na23, Fe57 were detected. The source of the single peak of Si28 is unknown. During the whole process (many sample positions), no other elements but calcium were detected.

The ring-shape part on the surface is the crater caused by the laser ablation of 7 pulses. The depth of the crater measured by AFM (Fig. 2) is about 2.76 μm and the diameter is about 20 μm. Roughly speaking, the depth of each ablation layer is about 400 nm.

3.2. SEM and EDX-analysis

The ring-shape crater from the LA-ICP-MS on the flat area of the cement paste was re-located under the SEM operated in low vacuum condition, as shown in Fig. 2. Position ‘a’ is the center of the crater and position ‘b’ is the nearby area on the same flat area. EDX-analysis was carried on these two spots. The spectra indicate the chemical compositions in these two spots to be identical. Back-scattering SEM image also shows the homogeneous chemical composition of the area. Both EDX analysis spectrums and back-scattering SEM images are coincident with the results from LA-ICP-MS. The massive (size of hundred microns) flat part area is concluded to be calcium hydroxide (CH) crystal.

3.3. AFM measurement on the hexagonal CH surface of cement paste

The cement paste dried in the N_2 was taken off the mica substrate and heated to 150°C for 2 hrs. The surface was measured by AFM in the glove-box filled with N_2. Fig. 3 shows the AFM image of the surface of the dried cement paste, with massive hexagonal crystals, which have been proved to be calcium hydroxide. Selected areas on such massive hexagonal crystal were investigated with AFM in different atmosphere.

3.4. Nanostructure of CH surface in different atmospheres

3.4.1. $N_2 + H_2O$

The moisture was introduced into the glove-box carried by nitrogen. The relative humidity was controlled to change with steps of 2–3%. The AFM images shown in Fig. 4 indicate the change of the surface structure with increasing humidity at the nanometer scale. At lower RH (<30%), the surface shows a smoothing effect and the main structure remains still unchanged (the height of the step in the center of image remains at about 13 nm). At about 30% RH, the sample was stored overnight: a smoother surface was found and the height of the step increased to about 16 nm. At higher RH (>41%), no stable image was obtained with the contact-mode AFM; the surface seems to become softer and possibly dissolved. We interpret the smoothing effect of CH crystal in the $N_2 + H_2O$ at lower RH and the instable image at RH > 41% to be because the surface of the CH crystal becomes softer or even dissolves with the condensation of the water film from the moist air. This interpretation is supported by the AFM investigation on molecularly thin films of water on mica by Hu *et al.* [10]. As shown by Hu *et al.* [10], the water vapor condenses to form a monolayer with apparent height of about 0.2 nm at 22%–28% RH (phase I water) while at 40%–50% RH the formation of a uniform ice bilayer (phase II water) has been observed.

3.4.2. $N_2 + CO_2$

A new sample of cement paste was dried and heated to 150°C for 2 hrs in N_2 before CO_2 was introduced into the glove-box (with a flow N_2/CO_2 ratio of 10:1). Fig. 5 shows the AFM image of a selected area of 3 microns on the big hexagonal crystal of Fig. 3 in pure N_2 and in $N_2 + CO_2$ for two days. No apparent changes of surface structure were found except some small grains become a little bit smaller (about 20–30 nm).

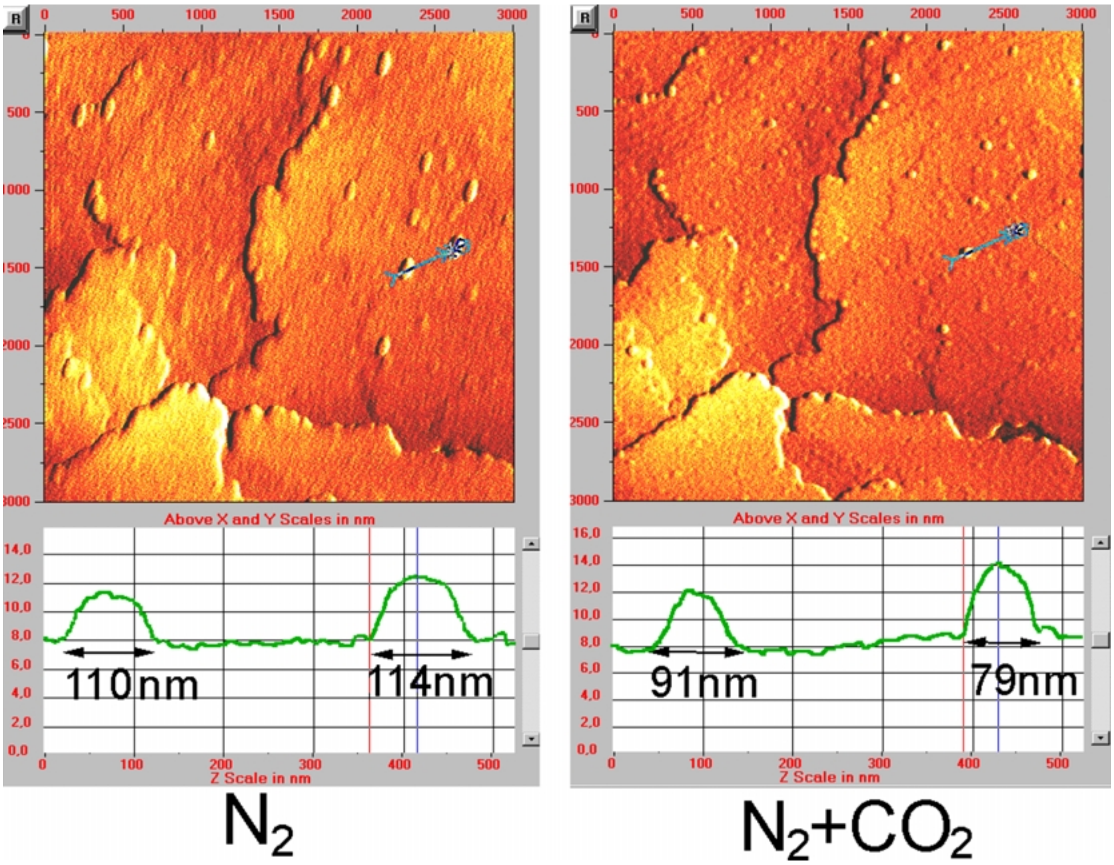
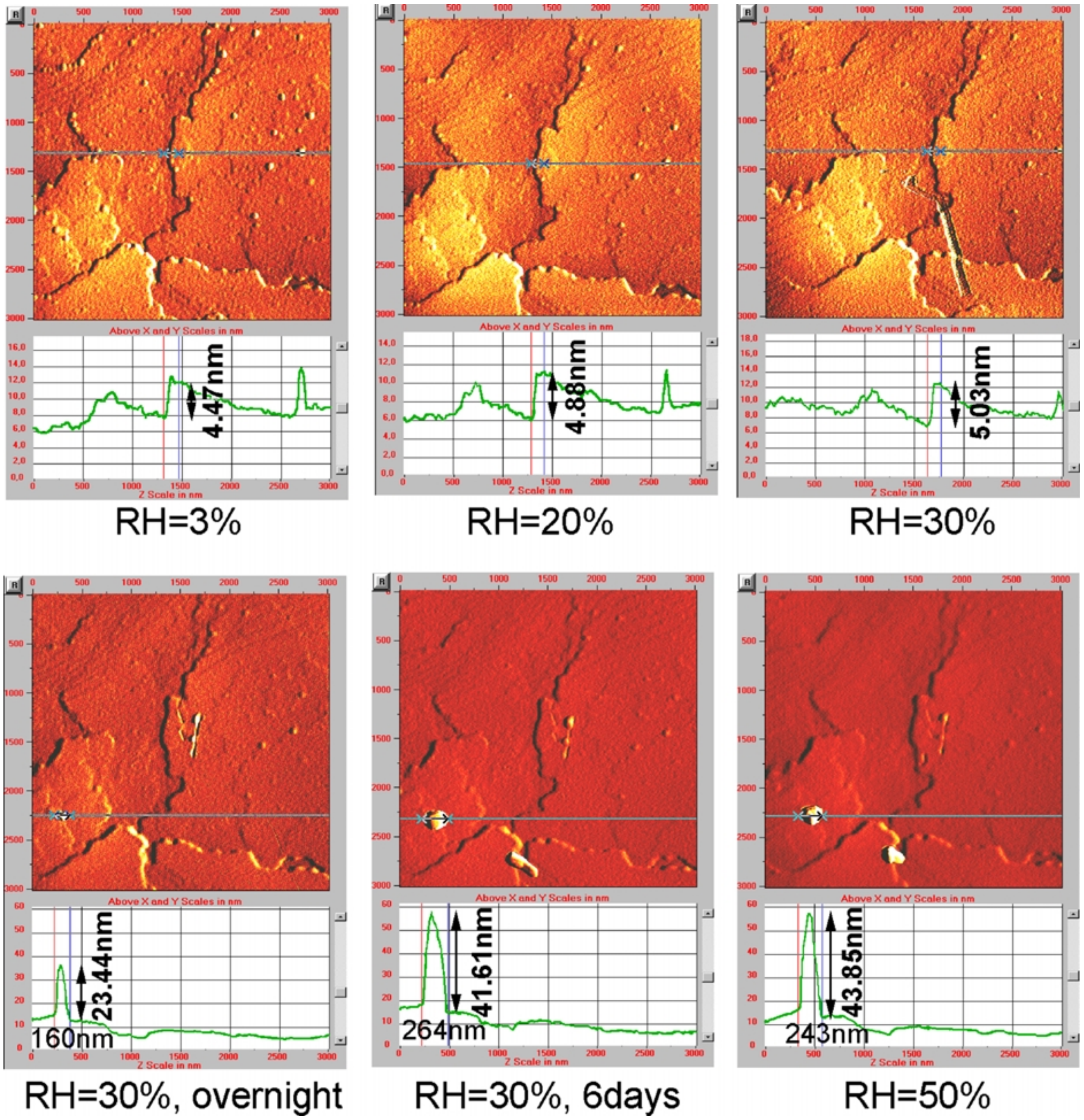


Figure 5 AFM images of the surface in $N_2 + CO_2$ atmosphere.



RH=3% RH=20% RH=30%

RH=30%, overnight RH=30%, 6days RH=50%

Figure 6 Surface structure changes with RH in $N_2 + CO_2 + H_2O$ atmosphere.

3.4.3. $N_2 + CO_2 + H_2O$

The flow of N_2 and CO_2 was fixed at ratio of 10:1 and the humidity was increased step by step by 2–3% RH. In Fig. 6, the surface structure remains unchanged at lower RH (<30%). At about 30% RH, movable particles were found on the surface, shown as a scratch in the middle of the image. It is a particle moved by the scanning tip of AFM and it was not found anymore in the second scan of the same spot. The sample was kept overnight at about 30%. Some small grains with size of about 160 nm size and height of 60 nm appeared on the surface. The measurement in some other places of the same sample reveal some movable grains starting to grow in such condition, as shown in Fig. 7. Some of the grains in the center of the image were moved away by the tip like a cleaning phenomenon, while others fixed on the surface and could not be moved by the tip. The atmosphere of $N_2 + CO_2 + H_2O$ with 30% RH was kept for 6 days, and the same spot was measured. Spherules were found to grow (as shown in Fig. 6, one selected spherule grows in size from 160 nm to 264 nm). The humidity was increased up to about 50% RH, no further change was found on this surface.

The observation of movable spherules in $N_2 + CO_2 + H_2O$ suggests the new phase on the surface starts to grow only when the CO_2 and H_2O are simultaneously present and when the moisture content is increased to a certain level (30% RH). It is possibly because $Ca(OH)_2$ is transformed to $CaCO_3$ in such conditions. It demonstrates the moisture to play an important role in the surface structure change. At lower RH, water vapor starts to condense and to form nano-droplets of water on the surface. The gaseous CO_2 is dissolved in the water nano-droplets to form aqueous H_2CO_3 and these provide suitable conditions for the carbonation of the $Ca(OH)_2$ to happen and form the movable spherules.

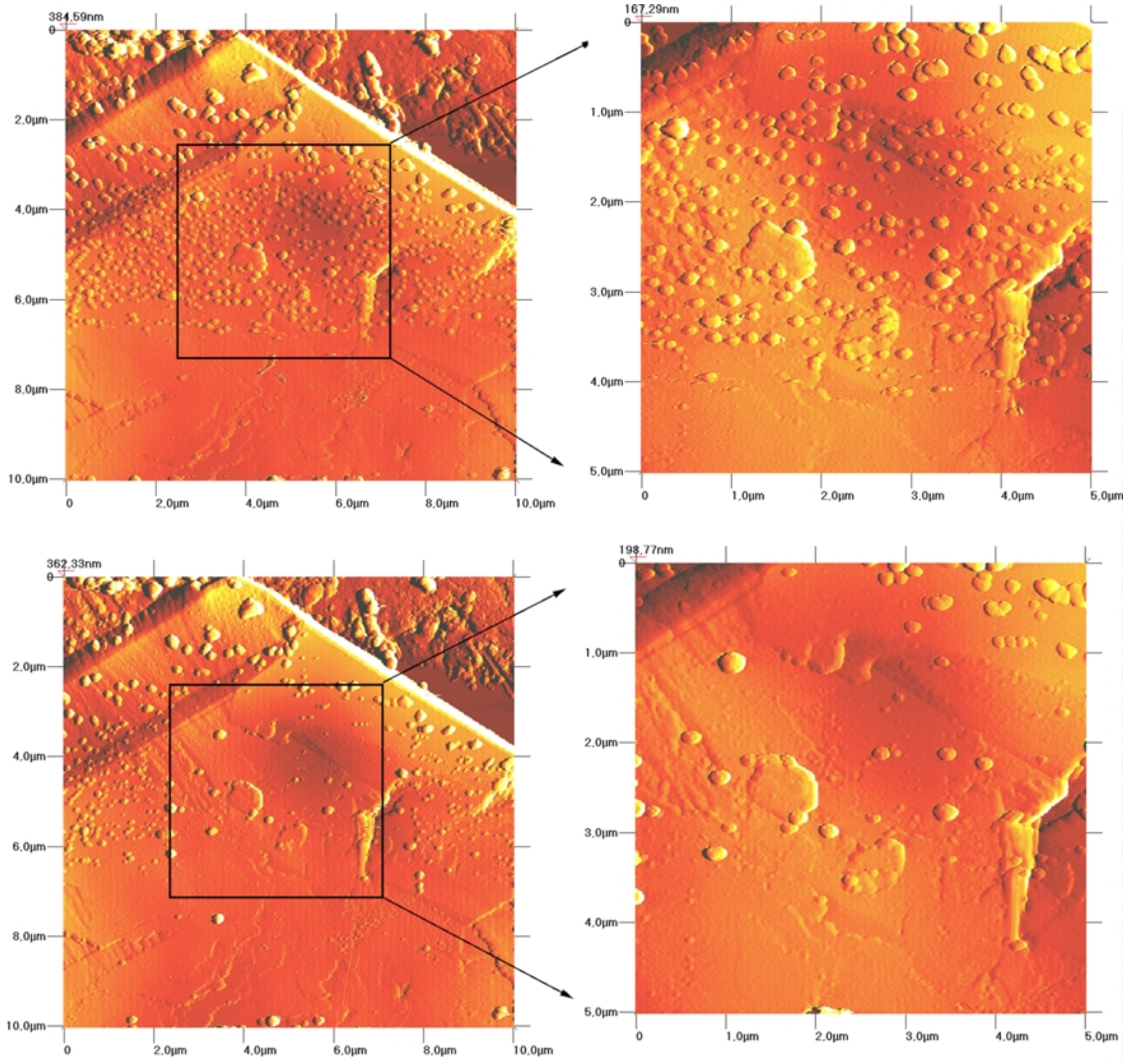


Figure 7 Movable spherules grow on surface in $N_2 + CO_2 + H_2O$ atmosphere at about 30% RH.

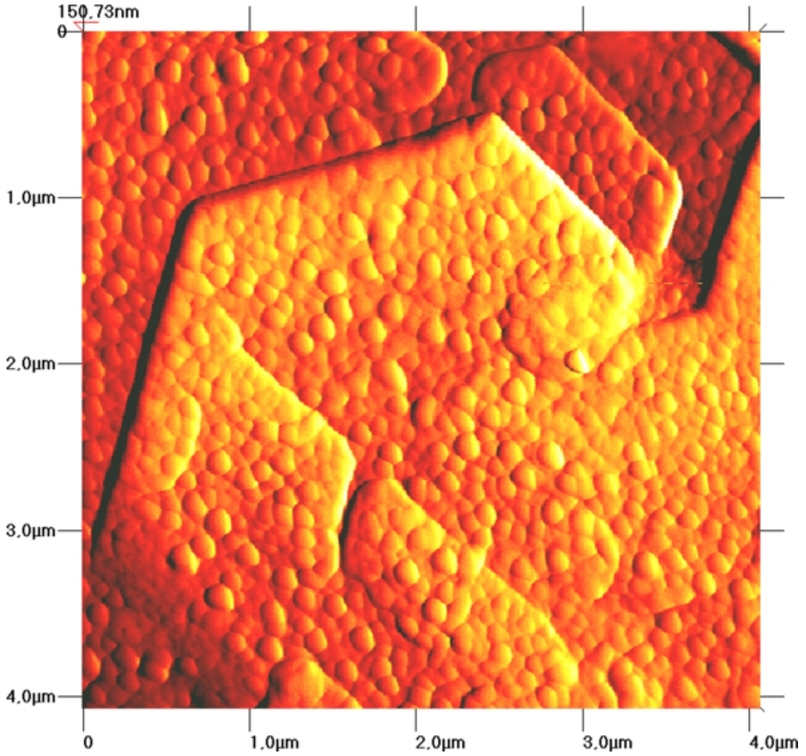


Figure 8 AFM image of surface of cement paste sample exposed to the ambient air for more than one year.

No instability of AFM measurement was found in the atmosphere of $N_2 + CO_2 + H_2O$ at about 40% RH. This can be due to the formation of the relatively dense $CaCO_3$ layer on the $Ca(OH)_2$ crystal, whose solubility in water is much lower than $Ca(OH)_2$.

When the cement paste prepared by MRM exposed in ambient air ($N_2 + O_2 + H_2O + CO_2$)for long term ($>$1 year), the surface was covered with a layer of spherules: Fig. 8. The spherules were found to be in the size of tens to hundreds of nm.

As reported by other investigators [1, 2–6, 21], during the carbonation process of cement paste, the formation of the microcrystalline $CaCO_3$ layers (as "vaterite" and "calcite") also could be observed by combined TEM, XRD and NMR.

4. Summary and conclusions

Cement paste prepared by MRM provided flat areas of calcium hydroxide for AFM investigation. The local chemical composition of such area was analyzed by LA-ICP-MS, SEM and EDX-analysis. Areas of sizes of hundreds of microns were identified to be actually calcium hydroxide crystals. In a pure N_2 atmosphere, $Ca(OH)_2$ shows a flat surface at the nanometer scale. This surface becomes soft with increasing moisture content. The occurrence of an instability at about 40% RH indicates the dissolution of the crystal surface. $Ca(OH)_2$ is transformed to $CaCO_3$ (and possibly $Ca(HCO_3)_2$) only if CO_2 and H_2O are simultaneously present. 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. With the aid of the AFM, the process of surface carbonation could be monitored directly and followed in real time. Although the information at the moment is still limited due to the full-contact mode of the AFM used, this experimental facility opens new ways for a comprehensive investigation of the carbonation as one of the main damaging mechanisms of the reinforced concrete structures.

Acknowledgements

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