INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS
J. Phys. D: Appl. Phys. **35** (2002) L25–L28 PII: S0022-3727(02)33006-7

## RAPID COMMUNICATION

# AFM investigation of cement paste in humid air at different relative humidities

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Received 24 January 2002
Published 2 April 2002
Online at stacks.iop.org/JPhysD/35/L25

**Abstract**
The surface structure of cement paste has been investigated in humid air by contact mode atomic force microscopy (AFM). The samples have been prepared by the novel mica-replication-method (MRM). For relative humidities between 3% and 20%, a structure change from coarse to fine grains has been recognized. Above this range no further significant changes were found.

## 1. Introduction

The most important building materials are porous: concrete/cement, brick, lime sandstone, etc. The heat and moisture transport in such materials play an important role for the durability of structures and therefore also for the sustainability of construction. Condensation damages, mould growth, etc give rise to sick buildings and costly repairs. For this reason, these processes have been investigated over a long time with various experimental methods as gravimetry, NMR, $\gamma$-absorption, etc but no molecular resolution was obtained. The description of such processes is mainly a phenomenological, thermodynamic approach and results in a system of coupled differential equations with some 'material constants' or functions of them (transport coefficients). The real physical information, however, is hidden in these phenomenological transport coefficients and up to now they are not well understood. A better understanding must consider the processes on a molecular scale.

Some basic ideas exist about the behaviour of water molecules in porous structures. There is a direct vapour diffusion in open internal spaces (pores), water film transport on the pore surfaces as well as a capillary transport. The three processes interact and are in a dynamic equilibrium with the surfaces involved. Any transport process in any porous material is thus basically governed by the structure and topology of the pores and the surfaces making up the pore boundaries.

Owing to the development of the scanning probe microscopy (SPM), the condensation and evaporation of molecular thin films of water on smooth surfaces could be investigated on a molecular scale. The mostly used SPM techniques include scanning polarization force microscopy (SPFM), non-contact mode and tapping-mode atomic force microscopy (AFM) [1–4].

Cement paste is a porous material with a complicated microstructure. In brief, it is composed of an amorphous phase (C–S–H gel), crystallites in the micrometre range and bound water [5, 6]. The surface of the paste is very rough and even a finely cut and polished sample is unsuitable for AFM investigations. Recently a special sample preparation technique, the mica-replication-method (MRM) [7], has been developed to obtain samples of cement paste with sufficiently flat surfaces. In this paper, the results of the first AFM investigations of the surface structure of cement paste in a humid air environment at different relative humidities are reported and discussed in some detail.

## 2. Experimental

The cement paste has been prepared by mixing portland cement powder with water of a water/cement ratio of 0.4 and put on a freshly cleaved mica surface. It has been aged under ambient conditions to complete the setting and hardening process. The paste has been taken off from mica and the surface facing to the mica, i.e. the replica of the cleaved mica surface has been investigated.

To see how the moisture acts on the surface layer of the replica, the sample was first dried by heating it up to 150°C under dry air with a relative humidity of $<3\%$ for 2 h. This drying procedure is equivalent to so-called 'D-drying'. The replica surface was then scanned under AFM.

The AFM measurements on the dried cement paste were performed in a humidity-controlled plastic glove-box. The ambient temperature was 20–25°C. The relative humidity (RH) in the box was controlled by adjusting the ratio of dry air to humid air (air bubbling through a wash flask filled with water), controlled by a dew-point hygrometer (Bruel & Kjar, Indoor Climate Analyzer Type1213, humidity transducer MM0037) with an accuracy of 1.0°C.

The AFM (Q-250, Quesant Instrument, California) was operated in contact mode, with the 40$\mu$m scanning head. In our situation, the electronic noise floor is in the 2–3 Å level. The tips are made of silicon, with a height of 10–15 $\mu$m, radii better than 10 nm and cone angle better than 20° at the apex. The force constant of the cantilever is about 0.2 N m$^{-1}$ and the resonant frequency is about 13 kHz. The scanning speed is 1 Hz and resolution is 400 × 400 pixel.

## 3. Results and discussion

Figure 1(*a*) shows the microstructure of the surface of the cement paste, scanned under dry conditions: RH of <3%. The paste is composed of clusters of grains with sizes in the range from 100 to 500 nm, $z$-heights from 4 to 20 nm. Such a structure is comparable with the description of Type III C–S–H phase as 'small equant grains' by Diamond [6] . When the RH increases to 20%, the microstructure of the surface changes progressively to that shown in figure 1(*b*). The big grains become smaller and the small ones on them disappear. The big initial grains have now sizes of only 200–300 nm and $z$-heights of 5–20 nm. No further change of the structure is found, when the humidity increases to 34% and 48%. The data of a statistical analysis of the samples shown in figure 1 are collected in table 1. The $z$-heights were determined over the whole sample (400 × 400 points) by digital image analysis

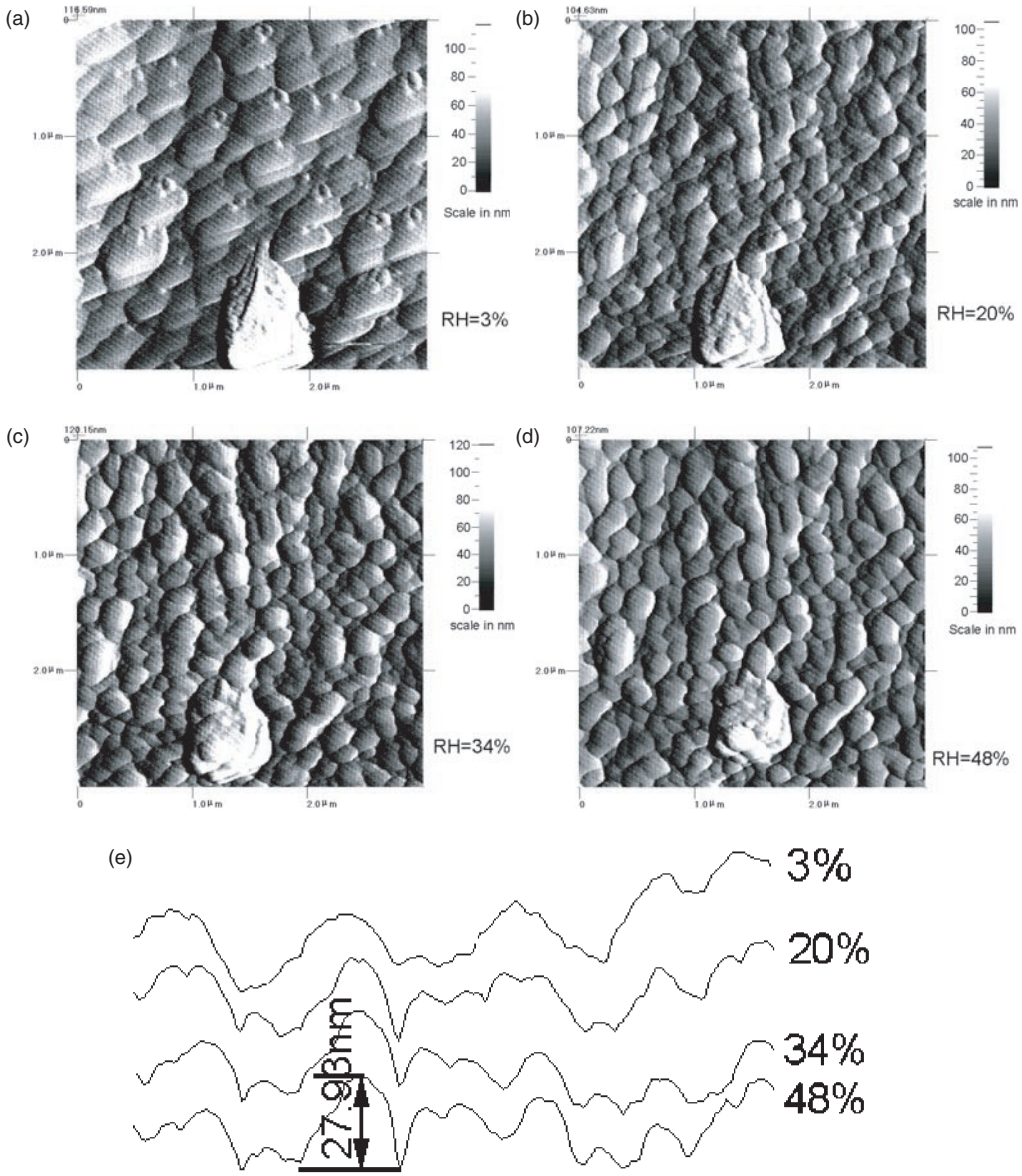


**Figure 1.** AFM images (3 × 3 $\mu$m) of cement paste in humid air of a given relative humidity: (*a*) RH = 3%, grains have sizes of 100–500 nm and $z$-height of 4–20 nm, (*b*) RH = 20%, grains have sizes of 200–300 nm and $z$-height of 5–20 nm, (*c*) RH = 34%, (*d*) RH = 48% and (*e*) profile curves of cross-sectional lines of the corresponding images.

by using a standard software package. The corresponding histograms are shown in figure 2 for four levels of relative humidity. The grain sizes were measured by hand (ten random profile lines across the sample). The average sizes of the grains change from 302.4 nm at 3% RH to 164.7 nm at 20% RH in horizontal direction, and from 217.9 nm at 3% RH to 174.5 nm at 20% RH in vertical direction.

When the relative humidity increases from 20% to 34%, there are still some small changes in the microstructure. As it was reported by Hu *et al* [1], the formation of phase I water mono-molecular thin layer was completed at humidities ranging from 22% to 28% [1]. Thus, the small change of microstructure may be because a thin water film could be formed on the surface of the grains and this could exert some pressure between the particles as well. This effect, however, is not very strong and the main structure of the surface remains unchanged.

The water meniscus formed between the tip and the surface while scanning at higher relative humidity could also be responsible for the small differences between the images. This interpretation is evidenced by the identical structure measured under RH = 48%, at which the phase II water film can also be formed to be a uniform layer (suggested to have ice-like bilayer structure [1]).

The true chemistry of the surface of cement paste obtained by the MRM (as described above) has not yet been identified. There remains a challenging task to elucidate to what extent the surface layer of the replica is a precipitation product of the cement gel and how far its grain structure has been induced via long-range forces by the mica surface itself.

To summarize, the AFM technique was introduced to the cement paste and measurements were carried out at different relative humidities. The sample preparation by MRM has played a key role in this approach. The results show the microstructure of the replica surface of cement paste to change at relatively low humidities. The process completes at about RH = 20% and no further change of structure could be detected when the humidity was increased.

**Table 1.** Data of statistical analysis of figures 1(*a*)–(*d*).

| | | Relative humidity (%) | | | |
|---|---|---|---|---|---|
| | | 3% | 20% | 34% | 48% |
| Grain size (horizontal) (nm) | Average value | 302.4 | 164.7 | 172.9 | 176.9 |
| | Standard deviation | 44.44 | 12.36 | 16.86 | 16.95 |
| Grain size (vertical) (nm) | Average value | 217.9 | 174.5 | 175.4 | 169.7 |
| | Standard deviation | 22.61 | 20.16 | 19.33 | 20.55 |
| *z*-height (nm) | Average value | 38.15 | 32.79 | 37.97 | 32.79 |
| | Standard deviation | 15.57 | 13.28 | 13.14 | 11.50 |

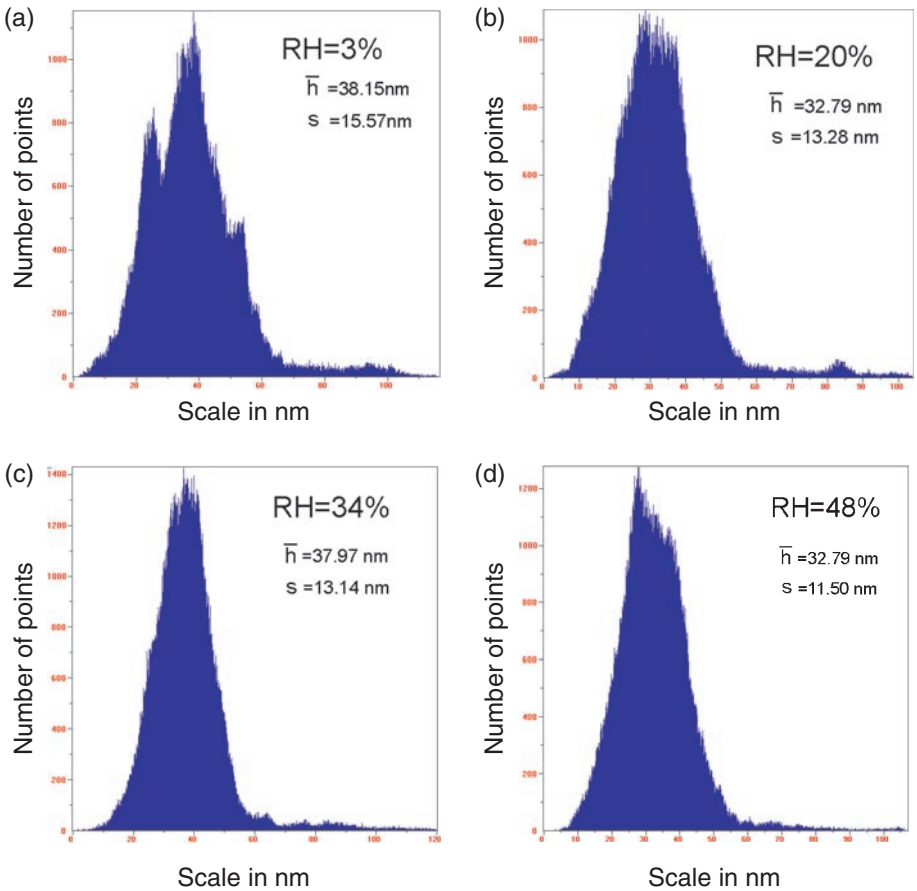


**Figure 2.** Histograms of the *z*-heights of the sample shown in figure 1. (*a*) RH = 3%: average height $\bar{h} = 38.15$ nm, standard deviation $s = 15.57$ nm; (*b*) RH = 20%: average height $\bar{h} = 32.79$ nm, standard deviation $s = 13.28$ nm; (*c*) RH = 34%: average height $\bar{h} = 37.97$ nm, standard deviation $s = 13.14$ nm; (*d*) RH = 48%: average height $\bar{h} = 32.79$ nm, standard deviation $s = 11.50$ nm.

Our further investigation will focus (i) on the process of water condensation and evaporation on the replica surface of the cement paste by using more sophisticated AFM instruments operated in Non-Contact or Tapping mode or SPFM and (ii) on the chemistry of the surface grains growing with increasing RH.

## Acknowledgments

The research work was supported by Top Nano 21 under No 5373.1. The IBWK institute at ETHZ, the ESEM center at EMPA and ETHZ, the AFM group of Prof. Ernst Meyer at the Physics Institute of University of Basel supported us in measurement and skill training.

*Note added in proof*

After the submission of this paper we became aware of the PhD thesis of D W Hadley: *The nature of the paste – aggregate interface* (Purdue University, 1972) where sample preparation techniques similar to our MRM have been described. In the meantime, the surface layer of the replica (analysed by laser ablation inductively coupled plasma spectroscopy) has been proven to consist of calcium hydroxide. We are indebted to Professor Detlef Günther of the ETH Zürich for his kind support in conducting these experiments.

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