Experimentální Analýza Napětí 2010
Experimental Stress Analysis

# Effect of surface treatment on the microstructure of cement paste assessed by AFM

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**Abstract:** This paper describes using of atomic force microscope for determination of the surface roughness and microstructural analysis of the cement paste surface. The microstructure of the sample surface is affected by many factors, e.g. preparation procedure, storage, water content and humidity of the surrounding environment. Roughness parameters as well as other microstructural characteristics were obtained for samples prepared with selected procedures and placed in different humidities. Increased humidity caused growth of hydration products on the surface and the roughness varied in time. Suitability of the preparation methods and the effect of humidity were evaluated in connection with other experimental techniques like nanoindentation.

**Keywords:** Atomic force microscope, Cement paste, Microstructure, Roughness, Humidity

## 1. Introduction

It is a doubtless fact that concrete and other cementitious composites based on cement binders belong to the most widespread structural materials all over the world. Its basic components are inexpensive and readily available in every corner of the globe. Currently, the world cement production is about 2.7 million tons per year. Despite of huge research in the past decades, a lot of mainly microstructural aspects are still uncovered due to the extreme complexity of the processes that take place in the cement microlevel. Therefore, there is a plenty of room for application of novel approaches.

The cement microstructure has a complex character. In contact with water cement hydrates and forms hydration products (cement paste). The solid part of cement paste components includes mainly calcium-silica-gels (C-S-H gels), $Ca(OH)_2$ (Porlandite) and the rest of unhydrated clinker minerals [1,2]. The microstructure contains also complicated pore structure (starting from gel nanoporosity to micrometer capillary and air pores) and water that is present in

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*Experimentální analýza napětí 2010*, Petr Šmíd, Pavel Horváth, Miroslav Hrabovský, eds.,
May 31 - June 3 2010, Velké Losiny, Czech Republic (Palacky University, Olomouc; Olomouc; 2010).

several forms – chemically bonded, adsorbed water and free capillary water [2,3]. Porosity and the presence of water influences both mechanical behavior as well as transport processes of the whole cement paste system. The development of the cement paste microstructure also depends on many factors, like chemical composition of the raw components, amount of mixing water, temperature, age, treatment and others.

Nowadays, there exist many experimental techniques that are able to access microlevel material properties. For example, electron microscope (ESEM) can be used for scanning of the sample surface topology and material composition, atomic force microscope (AFM) is used for the reconstruction of the surface morhology with nanometer accuracy. Moreover, micromechanical properties can be measured by means of nanoindentation [4] in volumes that start from nanometer level. All these techniques often rely on the fact that the sample surface is flat. Any surface roughness can disturb the measurement or distort the results. Therefore, it is necessary to monitor the surface roughness in these cases prior the measurements. The preparation of flat surfaces of cementitious samples was studied e.g. by Miller et al. [5] who developed automated procedure for sample polishing. Depending on the scanned area, the roughness was achieved in the range 20-50 nm.

Moreover, experimental measurement can be performed in different humidities that affect volume as well as surface of the sample. Therefore, our research was devoted to the monitoring of the humidity dependent microstructural changes on the cement paste surface. Many studies can be found for the effect of relative humidity to the shrinkage or porosity of the specimen. Only a few attempts are devoted to the effect of humidity to the surface roughness. For example, Keller et al. [6] studied the surface roughness of the cement surface prepared with mica replication method, i.e. cement cast on the mica plates in order to receive flat and pore-free surface. Then, this artificial surface was subjected to relative humidities in the range of 3 - 48% and the surface scanned with AFM. Keller et al. concluded that the major surface changes (increase in roughness) occur within the r.h. range of 3 - 20%. Larger humidities did not cause any substantial changes. However, the effect of time, i.e. duration of the exposition of the sample to humidity, was not considered in this study. It is, therefore, desirable to study the effect of humidity taking the exposition time into account.

## 2. Experimental part

### *2.1. Material and surface preparation*

This paper presents a case study of a cement paste prepared from ordinary Portland cement CEM I – 42,5 R (locality Mokrá, CZ) at the water to cement ratio of w/c = 0.4. Samples were cast to the plastic moulds (Ø 35 mm, h=70mm) and stored in water for approx. 10 months. After this period, high degree of hydration (over 90%) can be expected and the amount of unhydrated material in the cement paste microstructure is relatively low.

Before the experiment the samples were cut to 5 mm thick parallel slices and prepared with mechanical polishing. High precision diamond saw was used which resulted to the surface roughness of about 0.5-1 μm. Then, the surface was grinded on series of SiC papers (grit 2000 and 4000) and finally polished with 0.25 μm diamond suspension on polishing cloth in order to achieve as flat surface as possible.

*2.2. Atomic force microscope and the humidity chamber*

In this study all the surface measurements were performed with the aid of atomic force microscope (Dual scope DS 95-200, DME, Denmark). The AFM measurement is based on the mapping of the atomic force distribution over the sample surface. The sharp tip is brought close to the surface which generates attractive or repulsive inter-atomic forces. The forces cause deflection of the cantilever on which the tip is placed. The deflection is scanned with the precision laser sensor and subsequently the surface morphology is computed from this deflection. The resolution of AFM takes the order of 0.1 nm, i.e. atomic resolution. Two measurement types can be distinguished, the contact mode in which the distance between the tip and the surface is less then 1 nm and repulsive forces are generated or non-contact mode in which the distance is in the order of 1-10 nm and the forces are attractive [7]. Our measurements were performed in non-contact mode which is better suited for rough and highly disordered surfaces like cement paste.

For the measurement in different humidities, the AFM was installed in a custom made humidity enclosure capable of humidity control in the range of r.h. 5 - 95%.

*2.3. Experimental methodology*

Two types of samples further denoted as type O and F were prepared. Type O was taken just after the diamond saw cut without any further surface preparation. Samples of type F underwent further grinding and polishing as described previously.

First, the samples were taken out of the water bath and cut (time 0). Then, part of the samples (type F) was polished (time A). Slices were stored in the laboratory at 20 % r.h. for approx. 6 days. Next, the samples were systematically scanned with AFM and exposed to changing relative humidities in a humidity controlled chamber. After the first scan (time A), the samples were dried in temperature oven (at 50°C for 25-72 hours in order to achieve mass change less than 2%). It is supposed that a substantial amount of the evaporable pore water was released during this drying process from the samples (at least from the surface). After drying, the samples were placed in AFM, the chamber set to 8 % r.h. and scanned (time B and C). Then, the humidity was increased to 20% (time D and E), 30% (time F and G), 50% (time H and I) and in case of type F also to 85% (time J and K). All the time and humidity specifications are summarized in Tab. 1. The time course of the ambient humidity is shown for sample F in Fig.1.

AFM scans were performed on arbitrarily chosen rectangular area 30×30μm. The same place was scanned in all times in order to receive comparative roughness data. The roughness from the whole scanned area was evaluated using several parameters as described in the next section.

**Table 1. Measuring times and exposition to relative humidity**

| Measurement time notation | Sample O Time from cutting [h] | Sample F Time from cutting [h] | Conditions |
|---|---|---|---|
| **0** | 0 | 0 | sample cutting and polishing, 20% r.h. |
| **A** | 144,17 | 144,17 | measurement at 20% r.h. |
| **B** | 480,50 | 506,58 | drying, measurement at 8% r.h. |
| **C** | 480,83 | 507,08 | measurement at 8% r.h. |
| **D** | 481,25 | 507,58 | measurement at 20% r.h. |
| **E** | 481,58 | 508,08 | measurement at 20% r.h. |
| **F** | 482,42 | 508,58 | measurement at 30% r.h. |
| **G** | 493,67 | 528,33 | measurement at 30% r.h. |
| **H** | 494,92 | 530,33 | measurement at 50% r.h. |
| **I** | 501,58 | 553,58 | measurement at 50% r.h. |
| **J** | | 554,08 | measurement at 85% r.h. |
| **K** | | 560,33 | measurement at 85% r.h. |

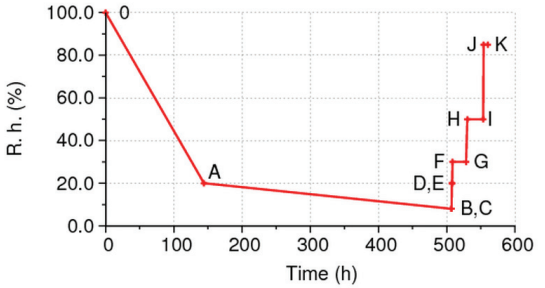



**Fig. 1.** Time course of the ambient relative humidity (sample F).

### *2.4. Surface roughness parameters*

The surface roughness can be characterized by many parameters. The proper choice of the parameter plays an important role in surface characterization and it depends e.g. on surface morphology (textured surfaces or disordered surface) and size of the scanning area (the parameters are usually size dependent) [5]. Some surface parameters are described in standards [8].

Due to the disordered nature of cement the best overall parameters are derived from average statistical descriptors. Based on previous studies we have selected the following three parameters. The Arithmetic mean deviation $S_a$ is defined as

$$S_a = \frac{1}{M \cdot N} \sum_{i=1}^{M} \sum_{j=1}^{N} \left| h_{ij} - \bar{h} \right| \tag{1}$$

the Root-mean-square deviation of the surface ($S_q$ or RMS) as

$$S_q = \sqrt{\frac{1}{M \cdot N} \sum_{i=1}^{M} \sum_{j=1}^{N} \left| h_{ij} - \bar{h} \right|^2}, \tag{2}$$

and the Ten-point-height $S_z$ is defined as the distance from the mean height of the five tallest summits to the mean depth of the five deepest valleys as

$$S_z = \frac{1}{5} \sum_{k=1}^{5} \left( h_k^{tallest} - h_k^{lowest} \right). \tag{3}$$

In the above equations, $M$ and $N$ stand for the number of measured points on AFM scan in two perpendicular directions $x$ and $y$, respectively, $h_{ij}$ is the height in a specific point *(i=1..N; j=1..M)* and $\bar{h}$ is the arithmetic mean from all heights.

### 3. Results and discussion

It is obvious that the surface treatment (i.e. mechanical polishing) influences the surface roughness in a straightforward way. Generally, the roughness characterized with average parameters ($S_a$, $S_q$) and measured for the saw cut (sample O) reaches values of $S_{a,q} \approx$ 300-400 nm. The roughness is decreased by polishing (sample F) to $S_{a,q} \approx$ 20-80 nm, see Tabs 2 and 3. This value is similar to that obtained by Yang et al. [6] ($S_q$=30-40 nm) for mica replicated samples. But there is a substantial difference between our samples that have surfaces opened from the material bulk and Yang et al. samples that are produced with artificial surface having the mica pattern. Our results correspond well with Miller et al. [5] who have received $S_q \approx$30-50 nm on similar samples and scanning area.

As follows from Tab. 2 for the O sample that the roughness slightly decreases with time and with increasing relative humidity. Perhaps, the reason is that large pores and surface valleys caused by saw cutting are filled with new hydration products on the freshly opened surfaces. Nevertheless, this fact can be tracked on point parameter ($S_z$) more than on average parameters ($S_a$, $S_z$) that remain more or less on the same level. Example of the surface scan of O sample is shown in Fig. 2. The graph showing the distribution of all heights in the image is depicted in Fig.3a (for every second time for clarity). As the time increases, the distribution curves are flattered compared to time A with a slight shift towards smaller heights. It is explained by the filling of the valleys by hydration products, rounding of the peaks and decreasing roughness.

The evolution of the F sample roughness is different compared to sample O. Both point ($S_z$) and average roughness ($S_a$, $S_z$) parameters are increasing in time and with increasing humidity as shown in Tab. 3. The reason is that new hydration products start to grow and form high peaks above the originally flat and polished surface. An example of the surface scan from the beginning of the measurement is shown in Fig. 4 with some small visible peaks that developed already before the first scan. Final scan in Fig. 5 clearly shows how the peaks increased their heights and volume after approx. 52 hours.

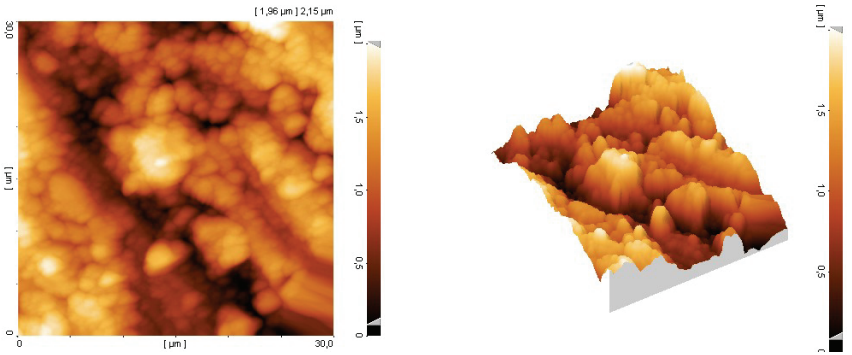
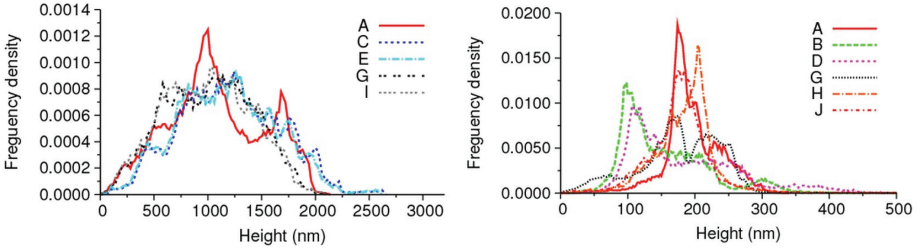



**Fig. 2.** Sample O as scanned with AFM (2D and 3D image) at 30% r.h., time G.

**Table 2. Surface roughness characteristics for sample O**

| Time | A | B | C | D | E | F | G | H | I | J | K |
|---|---|---|---|---|---|---|---|---|---|---|---|
| r.h. | 20% | 8% | | 20% | | 30% | | 50% | | 85% | |
| Time [h] from sample drying | | 0 | 0.33 | 0.75 | 1.08 | 1.92 | 13.17 | 14.42 | 21.08 | - | - |
| $S_z$ [nm] | 2060 ± 334 | 2970 | 2590 | 2560 | 2710 | 2690 | 1980 | 1940 | 1990 | - | - |
| $S_a$ [nm] | 375 ± 75 | 543 | 375 | 371 | 337 | 337 | 343 | 343 | 343 | - | - |
| $S_q$ [nm] | 453 ± 87 | 647 | 460 | 454 | 422 | 423 | 409 | 410 | 409 | - | - |




(a) (b)

**Fig. 3.** Frequency density plots of heights for sample O (left, a) and F (right, b).

The plot in Fig. 3b depicts the distribution of all heights in the image. The shift of curves towards higher values again shows on increasing roughness and the growth of the peaks. The frequency plot of F sample is much narrower compared to sample O due to much smaller roughness and thus the frequencies are also much larger.

**Table 3. Surface roughness characteristics for sample F**

| Time | A | B | C | D | E | F | G | H | I | J | K |
|---|---|---|---|---|---|---|---|---|---|---|---|
| r.h. | 20% | 8% | | 20% | | 30% | | 50% | | 85% | |
| Time [h] from sample drying | | 0.00 | 0.50 | 1.00 | 1.50 | 2.00 | 21.75 | 23.75 | 47.00 | 47.50 | 53.75 |
| $S_z$ [nm] | 214 ± 28 | 439 | 536 | 618 | 582 | 689 | 624 | 632 | 644 | 647 | 562 |
| $S_a$ [nm] | 18 ± 2 | 29 | 27 | 68 | 36 | 65 | 38 | 35 | 60 | 43 | 36 |
| $S_q$ [nm] | 25 ± 4 | 47 | 45 | 86 | 55 | 83 | 55 | 52 | 76 | 61 | 57 |

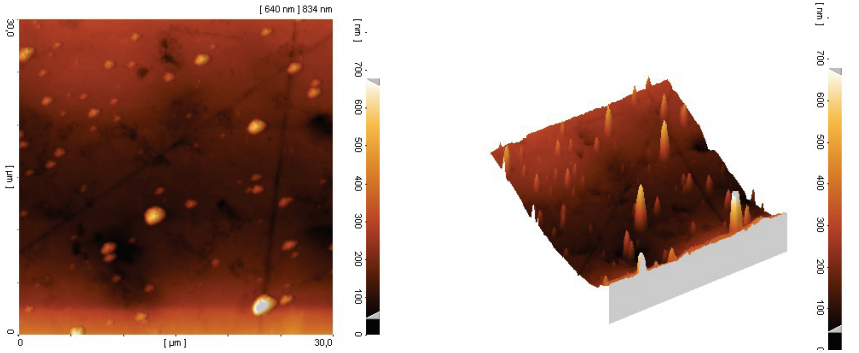



**Fig. 4.** Sample F as scanned with AFM (2D and 3D image) at 20% r.h. in time E.

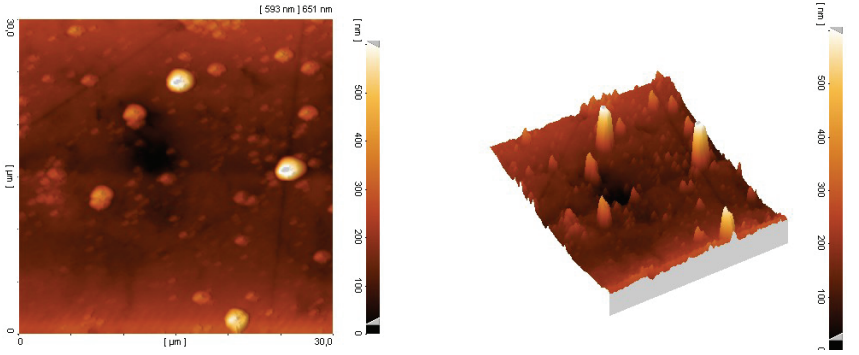



**Fig. 5.** Sample F as scanned with AFM (2D and 3D image) at 85 % r.h. in time K

## 4. Conclusions

Based on the AFM measurements of cement paste samples it was found that simple diamond saw cut does not produce surfaces suitable for further experimental techniques like ESEM or nanoindentation. It produces surface roughness in the order

of ≈300-400 nm (average parameters). Local roughness can be even much higher. Mechanical polishing can reduce the roughness to ≈20-80 nm. In humid air, the surface starts to change in time. New hydration products can either fill the valleys in case of originally rough sample (thus decrease the roughness) or can grow over the original surface and form solitary peaks (and thus increase the roughness).

The process of roughness change is accelerated by increased humidity and time. In case of samples F with originally flat surface, the resulting roughness was still acceptable e.g. for nanoindentation even after several days ($S_q$<80 nm).

**Acknowledgements**

The research has been supported by the Czech Science Foundation (GACR 103/09/1748) and Grant Agency of the Czech Academy of Sciences under Contract No. IAA200710801.

**References**

[1] Richardson G., "The nature of the hydration products in hardened cement pastes", *Cement and Concrete Composites*, **22**(2), pp. 97-113 (2000). ISSN 0958-9465.

[2] Taylor H.F.W., *Cement chemistry*, 2nd edition (Thomas Telford Services Ltd, London, 1997). ISBN 0 7277 2592 0.

[3] Hewlett P.C.,ed., *Lea's chemistry of cement and concrete*, (Elsevier, Oxford, 1998). ISBN 0 7506 6256 5.

[4] Fischer-Cripps A.C., *Nanoindentation* (Springer Verlag, 2002). ISBN 0-387-95394-9.

[5] Miller M., Bobko C., Vandamme M. and Ulm F.-J., "Surface roughness criteria for cement paste nanoindentation," *Cement and Concrete Research* **38**(4), pp. 467-476 (2008). ISSN 0008-8846.

[6] Yang T., Keller B. and Magyari E., "AFM investigation of cement paste in humid air at different relative humidities," *J. Phys. D: Appl. Phys.* **35**(8), pp. L25–L28 (2002). ISSN 0022-3727.

[7] Morita S., Wiesendanger R. and Meyer E., *Noncontact atomic force microscopy*, (Springer, Berlin, 2002). ISBN 3540431179.

[8] ISO 4287-1997. *Geometrical Product Specifications (GPS) - Surface texture: Profile method - Terms, definitions and surface texture parameters* (International Organization for Standardization, 1997).