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Atomic force and lateral force microscopy (AFM and LFM) examinations of cement and cement hydration products

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ABSTRACT

The objective of this work was to better understand how atomic force microscopy (AFM) and lateral force microscopy (LFM) techniques can be used as tools to understand the nanostructure and microstructure of cement and cement hydration products. AFM and LFM techniques were used on mortar samples to distinguish between CSH, CH, and unhydrated cement particles. The LFM technique appears to be more sensitive to topographic changes than conventional AFM and it can more clearly distinguish between the different phases at high magnification (low scan range). AFM could also be used to calculate the roughness of the interfacial transition zone (ITZ) between aggregate and the cement paste at different ages. The rough surface at the interface of the paste and aggregate is generally interpreted as higher porosity. It was found that a reduction in roughness (i.e., porosity) occurred for samples that were cured for a longer time which are consistent with the explanation of porosity.

1. Introduction

Cement-based materials are composed of amorphous phases, crystalline phases, water, and a wide range of pore sizes and shapes. Calcium-silicate-hydrate (CSH) is the dominant product of the hydration process, forming up to 60% of the hydrated cement paste volume. Calcium hydroxide crystals (CH) make up approximately 25% of the volume of the paste [1]. When aggregates are added to the paste the interfacial transition zone (ITZ) between aggregate and paste also influences the structure of the system on the nano and microscales. Since the nanoscale features are related to the performance and behavior of the material at the macro scale, resolving their structure at the nanoscale is helpful for understanding the behavior of hardened cement paste, mortar, and concrete.

Scanning electron microscopy (SEM) is used extensively to investigate the structure of cement-based materials at the microscale. Recently there is a growing interest to use scanning probe microscopes (SPMs) to study the micro and nanostructural characteristics of hardened cement-based materials. One of the methods that has recently been explored is the use of depth sensing micro-indentation for characterization elastic and fracture characteristics including its hardness, stiffness, and toughness [2–6]. Recently, atomic force microscopes (AFMs) have been used for the purpose of nanoindentation to determine mechanical characteristics at the nanoscale of cementitious materials (i.e., mainly the CSH phase) [5,7,8]. The AFM provides accurate positioning capabilities while offering a three dimensional image of the indentation impression. However indentation from AFM is typically performed at lower force levels than other indentation methods. Little work was done using AFM to characterize the micro and nanostructures including detailed morphology characteristics including the shape and size of features at the nanoscale of harden cement paste, mortar and concrete.

Atomic force microscopy (AFM) is a high resolution scanning probe microscope that can provide a topographical representation of a sample surface. Topographic images are obtained using a probe with a sharp tip at the end of cantilever. The tip of the cantilever is moved across the surface of a specimen. As this tip is brought into contact with the surface of the specimen the deflection of the tip can be measured and the topography of the surface is recorded [9]. By using this technique, AFM can provide detailed surface texture characteristics on particle shape for harden cement systems at a scale that cannot be provided by SEM [10–12]. Papadakis and Pedersen [10] found sufficient correlation between microscopic quantitative information provided by the AFM with

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macroscopic mechanical and durability parameters associated with cementitious products. Yang et al. [11,12] studied the surface structure of cement paste in humid air by AFM and noticed that the structure changes from coarse to fine grains as the humidity is changed.

Lateral force microscopy (LFM) is a derivative of AFM. In LFM the tip is maintained in contact with the sample surface and the 'twisting of the cantilever' is measured in addition to the vertical deflection (i.e., the approach that is more common for AFM). The detector on the cantilever arm collects a lateral deflection signal from the cantilever's twisting motion when it is used for LFM. The strength of the lateral deflection signal is related to the frictional force between the sample surface and the tip. Therefore the lateral deflection can be related to the friction of the surface. The LFM method is more sensitive to topographical variations than other methods. Until recently very little work has been reported on using the LFM technique to characterize the micro and nanostructures of harden cement-based materials.

The objective of this work was to understand how AFM and LFM techniques can be used as tools to provide insights on the structure of cement and cement hydration products. Mortar samples were prepared for this study. Two approaches were taken in the investigations using AFM and LFM. The first approach focused on investigating surface texture characteristics of hardened cement paste components such as CSH, CH and unhydrated cement particles using detailed images. The second approach focused on studying topographic differences at the aggregate cement paste interface (i.e., at the interfacial transition zone (ITZ)) due to different curing conditions. SEM and energy dispersive X-ray (EDX) were used to select appropriate regions for the AFM/LFM study to provide background information on the obtained images and surface characteristics.

2. Experimental study

2.1. Sample preparation

Mortar samples were prepared with a w/c (water to cement ratio) of 0.30 and 55% volume of natural fine aggregate (details are provided in Table 1 and Ref. [13]). The mortar samples were cast, sealed, and placed in an environmental chamber at 23 ± 1 °C until the samples reached an age of 1, 7 and 28 days. At each age of testing, the specimens were demolded and cut using a diamond tipped wafer saw with a low viscosity mineral oil as the coolant/lubricant. The mineral oil also helped to minimize additional hydration. The mortar slices were then immersed in acetone to remove the remaining free water and oil. After drying for several hours at room temperature the mortar slices were placed in a vacuum chamber for approximately 24 h and then placed in an oven at 50 °C for at least 3 days. The drying and oven conditioning steps were performed in an effort to remove the remaining free water from the pores to cease the hydration process. This was most important for the early age samples (i.e., the samples prepared at an age of 1 and 7 days).

After drying, the samples were ground with successive wheels of increasingly fine diamond paste (up to 0.25 μm) using low viscosity mineral oil (more details are provided in Refs. [13,14]). The polishing process was based on the method developed by Diamond [15]. The specimens were polished (without epoxy impregnation as the epoxy may penetrate into the cement paste pores, influencing the topographic characteristics measured by the AFM and even more by the LFM). To expose an un-carbonated area for investigation, the polished samples were cut into slices approximately 5 mm tall as required for positioning in the AFM, then cleaned in an ultrasonic acetone bath and stored in an oven at 50 ± 2 °C for several days until used under the AFM/LFM and SEM.

Table 1
Mixture proportions (in SSD).

Material	Proportions
Volume fraction of aggregates, %	55
w/c, by mass	0.3
Cement (kg/m^3)	727.0
Water (kg/m^3)	218.1
Aggregate (kg/m^3) SSD	1442.0
WRA (g/100 g cement)	0.6

2.2. AFM–LFM

The atomic force microscope used in this study was a Digital Instruments CP-II AFM system (manufactured by Veeco) with a silicon tip and a cantilever arm having the following dimensions: *T*: 3.5–4.5 μm, *L*: 515–535 μm and *W*: 30–40 μm, with a resonance frequency of 19–24 kHz, and 0.9 N/m spring constant. The microscope was operated in contact mode to provide topographic maps of the cement paste and mortar surfaces with a set point of 180 nN and scan speed of 0.5 Hz, using both AFM and LFM techniques. The tips were replaced frequently during scanning to avoid blunting while keeping high scanning resolution. During scanning the specimen was at room conditions (23 ± 2%, 45 ± 7% RH).

Different scan ranges of 50 μm, 15 μm, 10 μm and 3 μm and 1 μm were used in order to better understand the surface structure and particle shapes. The results shown in this paper consist of typical results obtained from these scans.

The regions used in the ITZ examination were selected after first using the optical microscope connected to the AFM to find the most interesting regions. Similarly, the region that was selected to study the hardened cement paste features was selected after performing SEM and EDX analysis as explained in the following section.

2.3. SEM–EDX

The scanning electron microscope (SEM) used in this study was a RJ Lee personal scanning electron microscope. The SEM was used in backscattered (B) mode with high vacuum condition to select the region to be scanned under the AFM. The goal was to select a typical zone of cement paste containing several features such as calcium hydroxide (CH), calcium silicate hydrates (CSH), and an un-hydrated cement particle. Energy dispersive X-ray (EDX) analysis was carried out to distinguish between the different features of the selected regions. The polished specimens were coated with a thin layer of palladium in order to observe these elements under the SEM. After the SEM observations and EDX analysis were performed, the coating was removed using acetone and the same specimen was immediately scanned using the AFM at the regions identified by the SEM and EDX. This was done to study the harden cement paste component characteristics.

3. Results and discussion

3.1. SEM–EDX

SEM BS observations were conducted on the entire surface area of the polished specimen to search for a region of the cement paste that can be scanned under the AFM and LFM. While numerous samples were examined, a typical region for a sample that was cured for 28 days is presented in Fig. 1a. This area was chosen to be scanned using the AFM and LFM as it contains several elements