Nanostructural Characterization 3D of Phases and Interfaces of Portland Cement Mortar

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Abstract: This paper proposes to go further in the characterization and micro nanostructural surfaces and interfaces of Portland cement mortars in a new way and the use of AFM (atomic force microscopy). The nanostructure of CSH (calcium silicate hydrate) has been the subject of much research, but it is still not clearly understood, some suggested models point ranging from colloidal “layers-sheets”. The AFM was used in this work in an unprecedented way for cementitious materials, in the case of this study, Portland cement mortars. There are no bibliographic reports of successful attempts to characterize these materials using such important technique to nanostructures. The preparation of the samples showed a positive surprise because as we had no previous parameters, we chose the simplest possible preparation that consisted of embedding a fragment of fractured mortar in bakelite and did the surface polishing. The topographic characterization is important because it shows the classical morphology of portlandite and calcite in the samples at the nanometer scale. These topographical micrographs and three-dimensional topographic profiles give us an exact picture of the morphology of cementitious materials in the interface ceramic block/mortar, interface roughcast mortar/mortar coating and top view of the mortar, being a powerful and effective characterization technique for micro and nanostructural.

Key words: Nanostructural characterization 3D, mortar, AFM, interfaces and surfaces, cementitious materials.

1. Introduction

The need for research and characterization of materials aimed at the construction has been growing due to the need for proper selection of materials, based on the performance of Portland cement based materials, as well as the increasing shortage of raw materials and market demand for products with adequate performance and durability. Only the evaluation of mechanical properties such as tensile strength tension of mortar is not enough to ensure proper performance of rendering mortar systems, especially in Portland cement materials that have micro and nanostructures still little explored. In this sense, this paper proposes to contribute to the microstructure characterization of micro/nanostructural aspects of Portland cement

mortars used for flooring in civil works using a new approach: by means of AFM (atomic force microscopy) as a tool for the characterization of Portland cement mortar.

2. Portland Cement Mortar

The rendering mortar more used in construction is composed of cement, aggregate and water, called cement mortar and cement, lime, aggregate and water, additives may be added to improve its characteristics. There is also a lime mortar composed only of lime, aggregate and water, which is little used nowadays.

2.1 Microstructure of Portland Cement Mortars

The main product of the hydration of Portland cement is an almost amorphous material—CSH (calcium silicate hydrate)—which represents about 60% by volume of paste. In chemical cement notation, CaO, SiO₂ and H₂O are represented by C, H and S, respectively. This compound has not a definite

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stoichiometry and is largely amorphous. CSH is often referred to as “CSH gel”.

The compound CSH is produced along with the calcium hydroxide in the chemical reaction of the silicate phases (β -C₂S and C₃S) with water. The compound CSH is the main binding agent in cement paste and is responsible for important properties such as strength and shrinkage. To search and characterize the structure of nanoscale materials is an essential part to understand and predict their behavior, and is also extremely important in the context of change and development of new systems of CSH [1].

The study of the structure of CSH in Portland cement systems using X-ray diffraction (DRX) is limited due to its poorly defined crystalline nature. Early studies were conducted using mainly the specific surface area, density measurements, and thermal analysis, as the first attempt to characterize this material [2, 3]. In recent decades, many new aspects of CSH were revealed with the advances in analytical techniques and application of new methods such as NMR (nuclear magnetic resonance) and AFM (atomic force microscopy), the latter is the subject of this research [1].

The nanostructure of CSH has been the subject of much research, but it is still not clearly understood. Some suggested models indicate the presence of colloidal “layers-sheets”.

One of the first models along this line has been proposed by Powers and Brownyard [4, 3]. It describes CSH as a colloidal material. In this model the gel particles are held together principally by van der Waals forces and the space between them is called “the gel porosity” which is only accessible by water molecules. A more comprehensive model was developed later by Feldman and Sereda based on extensive experimental studies of hydrated Portland cement systems, Feldman [5, 6]. The role of water in this model is explained in more detail and changes in mechanical properties of CSH related to water content can be more easily described.

2.2 AFM

The AFM can be considered as a hybrid between the equipment for measuring the force on surfaces (SFA), and a surface profilometer [7, 8]. The AFM can operate in the work scheme known as contact, similar to the profiler mode, but with much lower power load.

The AFM or SFM (scanning force microscope) can be operated in various ways. However, its basic principle is to measure the deflection of a cantilever with 100 to 200 μm in length, whose free extremity is mounted on the probe. These deflections are caused by forces acting between the probe and the sample [9].

When the probe approaches, the sample is first attracted by the surface due to a wide range of attractive forces existing in the region such as van der Waals forces. This attraction increases until the tip is very close to the sample, then, the atoms of the two masses are so close that their electronic orbitals begin to repel. This electrostatic repulsion weakens the attractive force as the distance decreases. The force vanishes when the distance between atoms is of the order of a few angstroms, the characteristic distance of the order of a chemical bond. When forces become positive, it can be said that the atoms of the tip and the sample are in contact and the repulsive forces eventually dominate [9].

Various types of forces contribute to the deflection of a cantilever in an AFM, as already mentioned [10].

To date there is no record of the use of atomic force microscope in research involving the characterization of masonry blocks used in construction, for this reason and for believing in the importance in investigative potential and uniqueness of this technique, this work has used AFM in the characterization of extremely small morphological aspects of the blocks and mortars under study.

3. Materials and Methods

Portland Cement Mortar Characterization of Portland Cement Mortar with the Use of AFM:

One of the main advantages of the technique of AFM is being able to work in different conditions and for studies of the properties of various materials in the ideal conditions for them, i.e. samples at atmospheric pressure, since no vacuum is needed, and especially in controlled environmental conditions.

Because it provides morphological 3D data, the technique allows analyzing the morphology, the microtopography and the geometric surface area, Vaz (1998), of solid samples. These factors help to study the physical characteristics and chemical reactivity of mineral phases, thus being able to control them through specific physicochemical procedures. Hence, mortar samples are analyzed by this technique in an unprecedented manner.

3.1 Microstructure of Portland Cement Mortars

The atomic force microscope used is installed in the Microscopy Center of UFMG, as follows:

(a) atomic force microscope—MFP-3D-SA ASYLUM RESEARCH—Modes Contact, Non-Contact and Semi-Contact (intermittent) in air; scan (x and y) of up to 90 micrometers, with isolation of vibration and external noise; nanoindentation.

3.2 Preparation of the Samples of Portland Cement Mortar

Three panels of masonry were built and mortar was applied over them with roughcast trait (1:3) of Portland cement and washed river sand: on top of these, three different coatings were further applied, one for each panel:

(a) a plaster cladding with stroke (1:6) of Portland cement and washed river sand; (b) a mortar coating (1:1:4) of cement, lime and sand; (c) a mortar lining with a stroke (1:2:8) of cement, lime and sand.

For sample preparation, approximately 12 cm × 12 cm pieces of the panels contained the complete system, ceramic block, roughcast mortar and mortar coatings. After the removal, the 12 cm × 12 cm samples were fragmented and reduced to approximately 6.5 cm. Sample fracture was used instead of cutting hard, not to interfere with the sample surfaces.

After being fragmented, the samples were prepared for analysis in the AFM. The preparation followed the basic procedures of ceramic/rock samples, that is, the mortar samples were impregnated within epoxy resin and then polished as seen in Fig. 1.

Fig. 1 Portland cement mortar samples prepared for AFM.

4. Experimental Results

From the analysis of the Portland cement mortars samples in the atomic force microscope micrographs such as Fig. 2a was obtained; this photo corresponds to the morphology of CSH present in the sample near the interface and in Fig. 2b, a group of ettringite crystals surfacing from inside a pore interface.

Fig. 3a shows the surface of the region near the ceramic block/mortar interface and Fig. 3b, the three-dimensional (3D) image of the topographic

profile shown in Fig. 3a. The morphology suggests portlandite and calcite.

Fig. 4a shows the topographic profile of the region near the ceramic block/mortar interface and Fig. 4b, the 3D version of the same region. The morphology clearly indicates oriented ettringite crystal groups.

A typical CSH area is seen in Fig. 5, showing very fine, colloform or botryoidal morphology. This aspect, consisting of minute spherules coalesced, is consistent with the amorphous nature of the CSH.

Fig. 2 Micrographs of the microtopographic profile of the region close to the ceramic block/mortar interface.

Fig. 3 Micrographs: (a) the microtopographic profile of the region close to the ceramic block/mortar interface; (b) 3D topographic profile of the region close to the ceramic block/mortar interface.

Fig. 4 Micrographs: (a) the microtopographic profile of the region close to the ceramic block/mortar interface; (b) 3D topographic profile of the same region.

Fig. 5 Micrographs: (a) the microtopographic profile of the region near the roughcast mortar/mortar plastering interface; (b) 3D topographic profile of the same region.

5. Conclusions

The AFM was used in this work in an unprecedented way for cementitious materials, here for Portland cement mortars. The samples preparation showed positive results, even though a simple procedure was used, which consisted of fracture mortar fragments impregnation in resin and doing the surface polishing.

The microtopographic characterization proved important because it showed the classical morphology of the important phases, such as ettringite, portlandite

and calcite in the samples at the nanometer scale. Also, the typical morphology indicates CSH, as very fine, colloform or botryoidal morphology. This aspect, consisting of minute spherules coalesced, is consistent with the amorphous nature of the CSH and is harder to be observed with other microscopy methods like scanning electron microscopy.

These microtopography micrographs and the corresponding three-dimensional profiles have provided very good morphological pictures of the cementitious materials at the ceramic block/mortar interface and at the equivalent roughcast

mortar/rendering mortar. Therefore, the ATM technique demonstrated to be a powerful and effective tool for micro and nanostructural characterization for the Portland-based materials.

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