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Cement and Concrete Research 37 (2007) 32–37
Cement and Concrete Research

A novel system for in-situ observations of early hydration reactions in wet conditions in conventional SEM

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Received 16 December 2005; accepted 18 September 2006

Abstract

A novel system enabling wet microscopy in conventional SEM is described and its performance for in-situ study of hydration reactions is demonstrated. The technology is based on a sealed specimen capsule, which is protected from the microscope vacuum by an electron-transparent partition membrane. Thus, the wet sample can be placed and observed in a "conventional" SEM without the need for drying or employing environmental SEM. Early hydration reactions of gypsum and cement systems were followed during the first 24 h.

Keywords: Wet SEM; In-situ SEM; Early hydration reactions

1. Introduction

The early age hydration reactions of cementitious systems are crucial elements in controlling early age properties such as workability retention and setting and they have significant impact on the properties of the hardened material, since at this stage the template of the mature hardened microstructure is being set. Numerous techniques have been employed to follow the early age hydration reactions within the time frame of several minutes up to 24 h. At this stage the reactions are more intense in their rates as well as in the changing nature of the hydration products. Analytical techniques such as X-ray diffraction and thermal analysis can be used to quantify the composition of the hydration products, while microscopy enables a view of the microstructure to be obtained. Ideally, one would like to follow the formation of the morphology at this stage continuously, by making in-situ observations in electron microscope. However, this is not possible in "conventional" electron microscopy because of the need for drying the sample. The use of environmental electron microscope eliminates this need [1–9], but such microscopes are not readily available and maintaining fully sealed conditions, as close as possible to 100%RH, is not always straightforward. More than that, for hydration to take place the cement grains must be immersed in water, and thus the microscope will only image the surface of the water.

This paper presents a novel technology which allows the observation of wet samples in the electron microscope, whereby the sample is kept sealed in a special cell which can be placed in the microscope chamber. The system was evaluated in preliminary testing of gypsum and Portland cement systems.

2. The wet cell system

The WETSEM™ is a novel enabling technology that allows direct observation of samples in their original wet state, using a conventional scanning electron microscope. The sample is placed in a sealed specimen capsule (Fig. 1a), and is protected from the microscope vacuum by an electron-transparent partition membrane. Thus, the wet sample can be placed and observed in a "conventional" SEM without the need for drying or use of an environmental SEM. The thin membrane is used as a window through which imaging and X-ray analysis is carried out. Imaging is performed using a standard Scanning Electron Microscope (SEM) combined with a Back Scattered Electron (BSE) detector (Fig. 1b).

Details of the method and the membrane which were developed by Quanomix Ltd, Israel, are provided in US patent 6992300 (January 1st, 2006). The capsule is essentially a cylindrical sample cell which is sealed on its top with a transparent membrane

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doi:10.1016/j.cemconres.2006.09.014

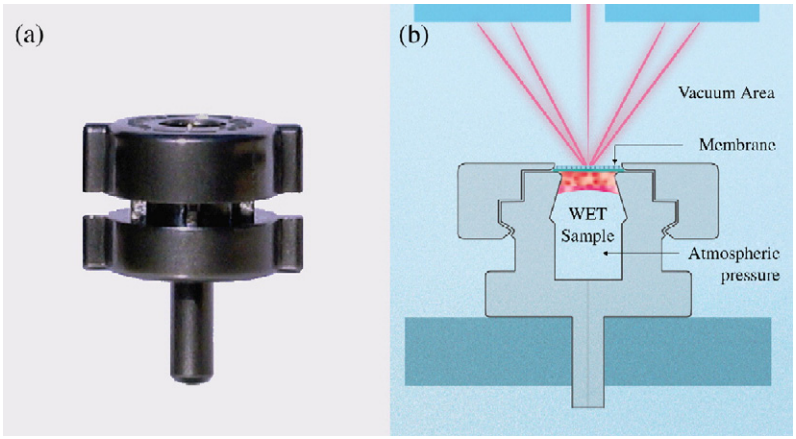

Fig. 1. WETSEM™ wet cell technology: (a) Quantomix capsules QX-102 and QX-200C; (b) Schematic representation of WETSEM™. (25 min) (33 min) (41 min) (49 min) (57 min) (65 min).

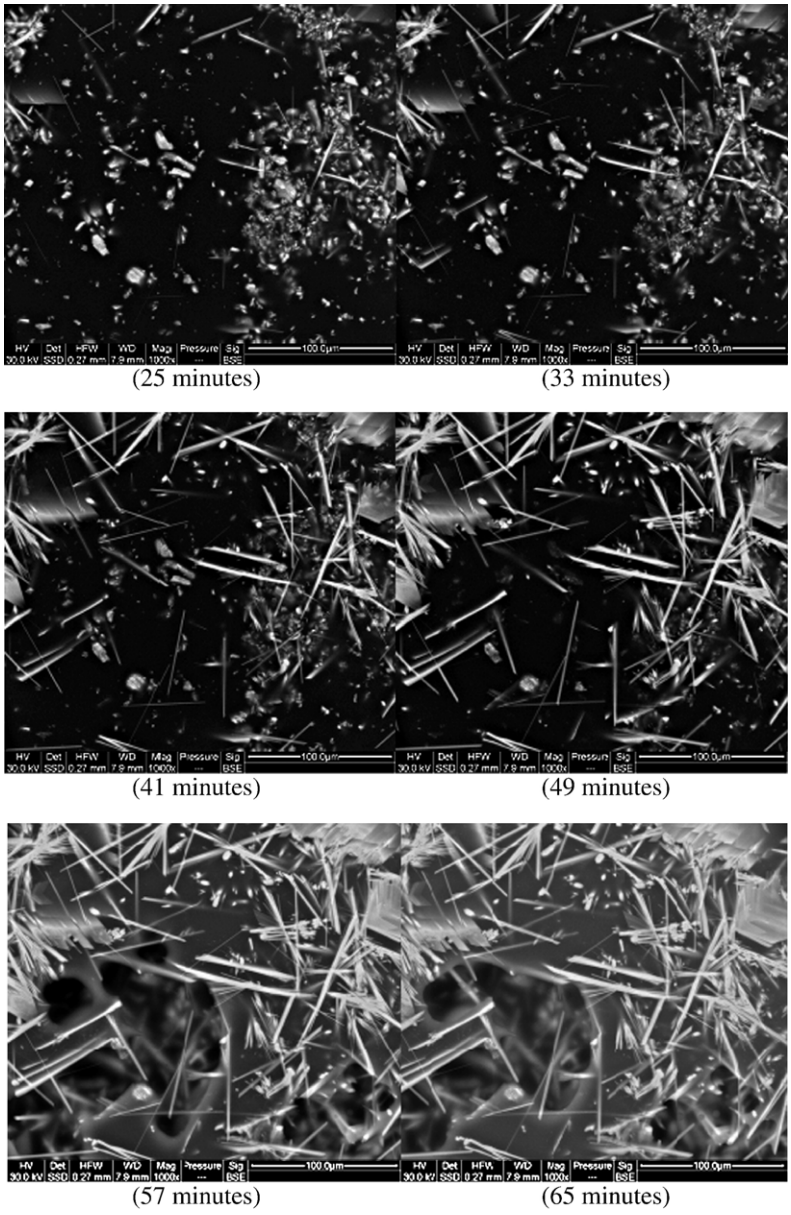

Fig. 2. The development of the microstructure of 0.6 water/binder ratio gypsum paste during the first hour. (a) 1 h (b) 6 h (c) 24 h.

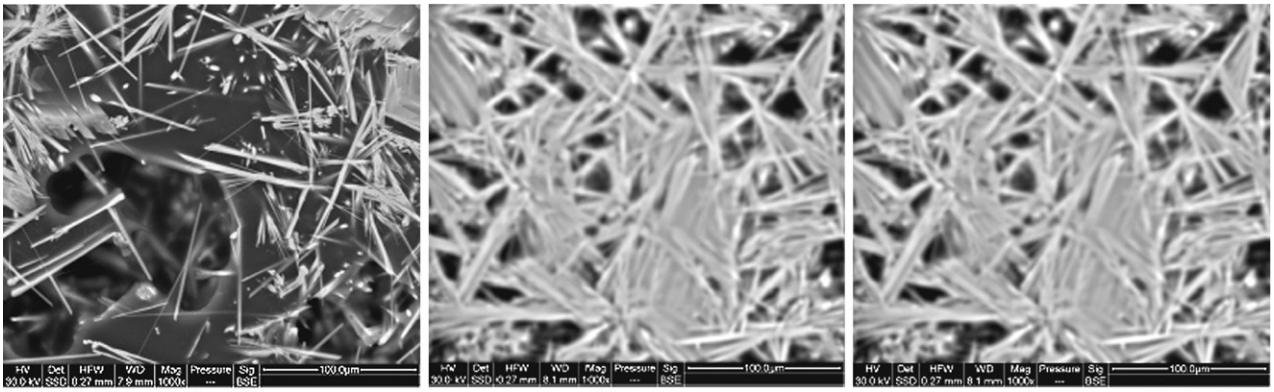

Fig. 3. Observations of gypsum paste (0.6 water/binder ratio) at 1 to 24 h, at magnification of 1000.

supported by a metal grid. The membrane is able to withstand a pressure difference of about 1 atm, between the vacuum of the electron microscope and the environment within the wet sample sealed by the membrane. The membrane is however thin enough for the electrons to pass through and interact with the sample within the cell and for backscattered electrons (BSE) to be detected. The membrane is of sufficient electrical conductivity to prevent local charging of its external surface, which may perturb the incident electron beam and blur the image.

The specially modified capsule QX-202C which is compatible with cement and other hydraulic materials was used in this study. It will be referred to as the "capsule."

Potentially, this type of technique seems to be particularly attractive for studying early hydration reactions, where a paste consisting of a mix of binder and water is cast into the cell and placed in the SEM to follow hydration reactions, in particular during the first 24 h, where setting and hardening occur, and where the reaction is most rapid and accompanied by significant change in the nature of hydration products. In Portland cement system this will include early formation of crystalline products (e.g. ettringite) accompanied later on by the formation of crystalline monosulfate and calcium hydroxide as well as amorphous C–S–H gel. Other cementitious systems, such as alumina cement and rapid hardening cement will also show early age development of different crystalline products and amorphous ones, whereas gypsum will develop only crystalline hydration products.

3. Experimental

In order to explore the feasibility of this system, the hydration reactions over 24 h of Portland cement and gypsum pastes were studied. Gypsum reacts quite fast, and its products are crystalline. Thus, this system can serve as a model "clean" system to explore the efficiency of using the capsule, because of its fast hydration reactions and the crystalline nature of its products, which can be more readily observed and resolved.

The paste samples were prepared at two water/binder ratios: 0.4 and 0.6 for the Portland cement and gypsum, respectively, representing practical paste compositions, and higher water/binder ratio of 0.9 (for the Portland cement) in which the microstructure to be developed is expected to be more open, and the resolution improved.

The SEM used for the observations in this work was Quanta 200 made by FEI, with the tests being conducted at 25–30 kV and working distance of 8–10 mm.

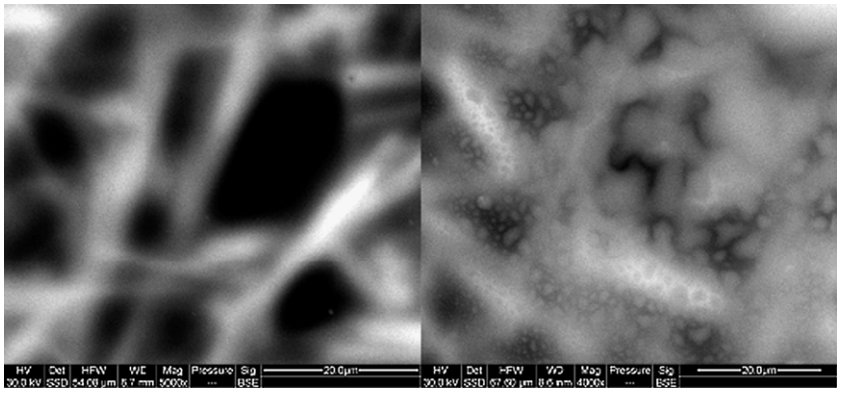

Fig. 4. Observations of gypsum paste (0.6 water/binder ratio) at 3 h at magnifications of 4000×; left-short term observation, right-longer term observation (a) 600× (b) 2500×.

4. Gypsum system

4.1. Gypsum during the first hour

The observations initiated 17 min after mixing with water and a sequence of micrographs at 1000× magnification was taken (Fig. 2). At 25 min unreacted grains can be seen dispersed in water with a few needle-like crystals, whose growth can be followed in the micrographs taken at later stages. The formation of a network of gypsum crystals is evident within the first hour of observation. Starting at 57 min, a cavity can be observed on the bottom left side. The cavity may represent a space which was initially filled with water, and it was desiccated as the water was consumed in the hydration process.

Some of the needle-like crystals can be seen at a much better resolution than others, and these may represent the ones closer to the membrane, or even ones which may have deposited on the membrane.

4.2. Gypsum at 1 to 24 h

Typical observations in the time period between 1 and 24 h are presented in Fig. 3 showing the characteristic gypsum microstructure of a network of needle-like crystals forming a dense mesh with pores in between them. The space occupied by the solid material in between the pores seems to consist of a mass of individual needle-like crystals, which are clustered together. Some of these crystals are seen at a higher resolution, and as suggested before, there may be ones closer to the membrane, or even deposited on it.

It was noticed that when the beam was placed on the same zone at higher magnification, the microstructure observed seemed to be undergoing a drastic change within few minutes (Fig. 4). Since this time period is too short for a change in the microstructure due to additional hydration, the changes observed might be induced by local heating which leads to partial decomposition of the gypsum.

The observations reported here are consistent with the current know-how of the hydration and microstructure formation of gypsum systems, which are forming when gypsum hemi-hydrate is reacting with water. It was possible to resolve the formation over time of the individual gypsum crystals, and the formation of the typical network of needle-like crystals network characteristic of the gypsum microstructure.

5. Cement system

5.1. Water/binder ratio of 0.40

There was a difficulty observing the individual cement grains at the early ages of 3 h (Fig. 5) and this may be the result of adsorption of water on them. Also, the grains were not uniformly dispersed and this may be associated with the hand mixing of a small sample.

At 24 h hydration products can be seen to develop, and zones of massive and dense material can be observed with pores in between them (Fig. 6). At higher magnifications two types of

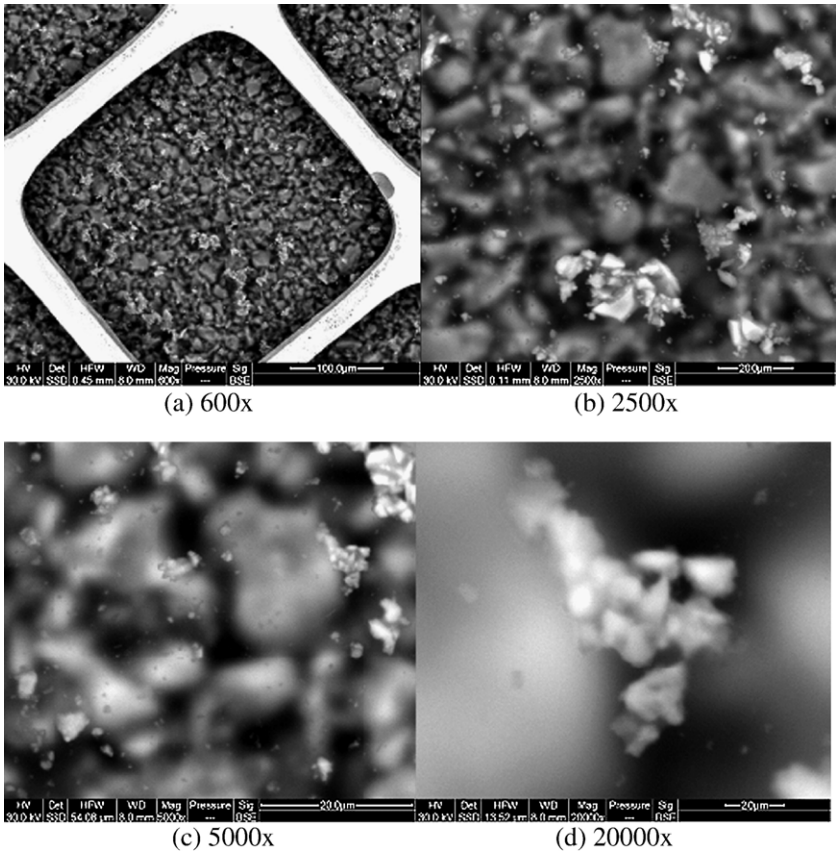

Fig. 5. Observations of cement paste of 0.4 water/binder ratio at 3 h at different magnifications. (a) 600× (b) 2500× (c) 2500× (d) 20,000×.

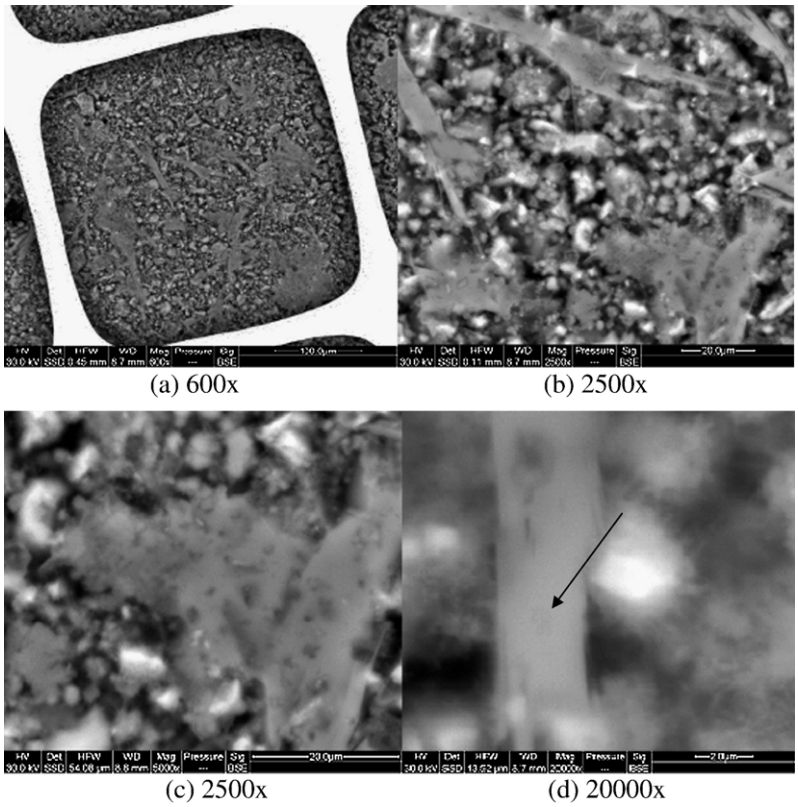

Fig. 6. Observations of cement paste of 0.4 water/binder ratio at 24 hours at different magnifications. The EDS of the massive linear structures in (d), marked by arrow, indicates calcium hydroxide composition. (a) 2500× (b) 5000× (c) 2500× (d) 2500×.

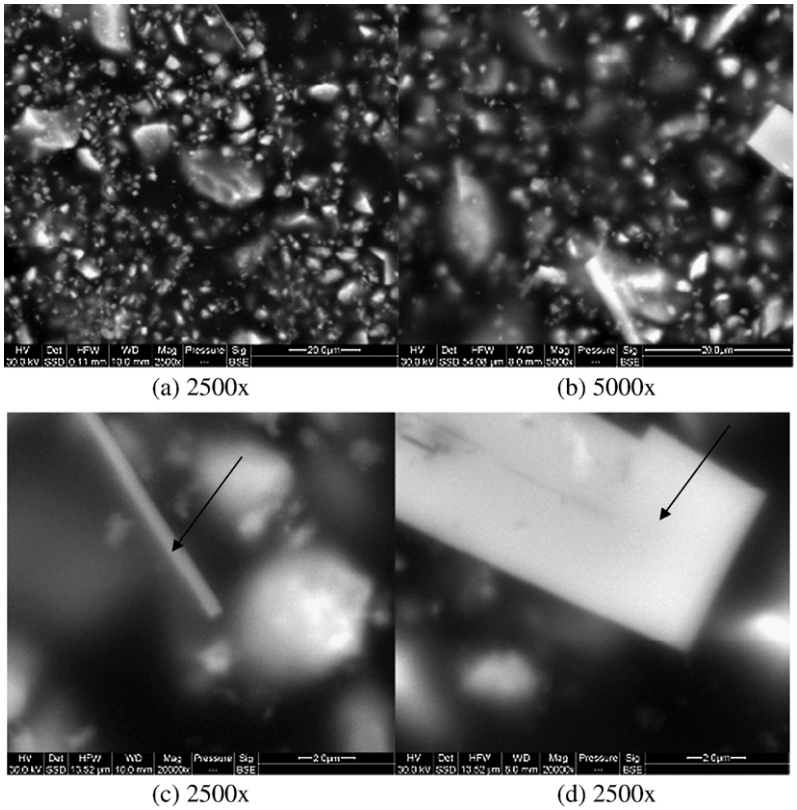

Fig. 7. Observations of cement paste of 0.9 water/binder ratio at 6 h at different magnifications. The more massive linear structures, marked by arrows in (c) and (d), are calcium hydroxide crystals.

microstructures can be seen, one which is more globular in nature, apparently C–S–H formed around cement grains, and the other more massive and linear, apparently calcium hydroxide crystals, as indicated by EDS measurements (Fig. 6d). A fuzzy morphology of acicular hydration products at the edges of the "globules" can be observed (Fig. 6d), a morphology which is similar to the outer products, as reported for example by Richardson using TEM techniques [10].

5.2. Water/binder ratio of 0.9

Observations at 6 h (Fig. 7) show a similar morphology as the 0.4 water/binder ratio, but somewhat more open. Here too, some more massive linear products are observed, and EDS analysis suggest that they are calcium hydroxide crystals (Fig. 7c and d). The resolution at magnifications of 2500× and above, which is required for this kind of observations, is rather limited.

6. Conclusions

- The samples could be readily made in the wet cell and observed in the SEM without any accompanied problems in the SEM operation.
- The early age study of the gypsum system could clearly resolve the development over time of the gypsum crystals, in terms of their first appearance, growth in length and widening, including the formation of a mesh of gypsum crystals. The resolution was reasonable, but there is room for improvement.
- The more mature gypsum system showed the familiar microstructure of a dense network of crystals interwounded together in a relatively dense microstructure with spaces observed between the crystals. However, the microstructure seemed to be two-dimensional, bringing up the issue of whether there is a preferred deposition/growth of hydration products on the polymer film of the cell.
- The hydration products of the cement seem to have the meshy structure typical to amorphous C–S–H. Observations at higher magnifications could reveal grains engulfed with tiny needle-like structure which may represent the outer hydration products. There is room to explore here the feasibility of improvement of the resolution.
- Crystals could be observed in the hydrated cement samples, and they were identified by EDS as calcium hydroxide crystals. However, they seemed to have a preferred orientation, where the *c*-axis (of what is presumably a plate-like crystal) is parallel to the membrane. This, and some other observations of hydration products bring up again the issue of preferred growth/deposition of hydration products on the membrane.
- Observations at higher magnifications (over 10,000×) or prolonged exposure seemed to have resulted in decomposition of gypsum crystals. This may be the result of the locally high temperature, and one may expect this to happen also with ettringite that decomposes at relatively low temperatures compared to other hydration products.

Acknowledgement

The authors express their thanks to Quantomix Ltd. for the technical support and discussions. The guidance of Mr. Ofer Zrihan in carrying in the specimen preparation and testing is highly appreciated.

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