

# A Capsule for Dynamic In-Situ Studies of Hydration Processes by Conventional SEM

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## BIOGRAPHY

Irit Ruach-Nir obtained her PhD in chemistry at the Department of Materials and Interfaces of The Weizmann Institute of Science in Rehovot, Israel. Since 2004 she has worked for QuantomiX as chief chemist on application development and on research of new applications in the field of materials science.



## ABSTRACT

This article describes a novel technology that enables the imaging of wet samples inside a scanning electron microscope. The technology is based on the separation of the sample from the vacuum by an electron-transparent yet robust membrane. The sample is placed inside a vacuum tight capsule, thereby enabling in-situ studies of dynamic processes, such as cement or gypsum hydration, inside a conventional SEM. Wet mixtures of binders were placed in the sealed specimen capsules, specially designed for long studies inside the microscope chamber. The samples were imaged using a SEM operating in high-vacuum mode and the hydration reactions were followed.

## KEYWORDS

scanning electron microscopy, backscattered electron imaging, energy-dispersive X-ray spectroscopy, in-situ chamber, wet samples, cement, hydration reactions

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## INTRODUCTION

Wet-SEM technology is a novel method that enables the imaging of fully hydrated samples in a scanning electron microscope. It is based on a vacuum-tight capsule (Figure 1a) with an electron-transparent window; a wet sample is placed in the capsule and observed in a conventional SEM (Figure 1b). The imaging method is based on the detection of backscattered electrons which result only from interactions of the electron beam with the thin layer of the specimen closest to the transparent window. As there is no requirement for sectioning, drying, freezing or using low-pressure or environmental SEM, sample preparation is both simple and rapid. The wet-SEM method is suitable for a wide range of applications in the materials and biomedical sciences [1-4].

### Applications to cementitious systems

Electron microscopy is one of the most important tools for the characterization of microstructures in cementitious and gypsum systems. However, the vacuum inside the microscope chamber makes it unsuitable for following dynamic processes, such as hydration reactions. Water loss from hydrated specimens cannot be completely avoided even when using the environmental SEM. The new wet-SEM capsule was specially developed for prolonged studies inside the vacuum chamber of the microscope. This capsule, in which the sample is kept under atmospheric pressure and fully wet, enables the in-situ study of the dynamics of processes such as hydration, inside the electron microscope [5,6].

The initial chemical composition of cement is complex as is the dynamic behavior of the hydration process. Both aspects are not well

understood at a fundamental level. A better understanding of the early stages is needed in order to improve performance and to develop specialty application cements. Cement powder consists of multi-size, multi-phase, irregularly shaped particles generally ranging in size from less than 1  $\mu\text{m}$  to slightly more than 100  $\mu\text{m}$ . When this starting material is mixed with water, hydration reactions occur which ultimately convert the water-cement suspension into a rigid porous material, which serves as the matrix phase for concrete. The various chemical phases in the cement powder hydrate at different rates and interact to form various reaction products. Typical Portland cement is composed of 50%  $3\text{CaO}\cdot\text{SiO}_2$ , 25%  $2\text{CaO}\cdot\text{SiO}_2$ , 10%  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ , 10%  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$  and 5%  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ . Only the calcium silicates contribute to strength. Upon the addition of water, tricalcium silicate, which is responsible for most of the early strength, rapidly reacts to produce calcium ions and hydroxide ions. Dicalcium silicate, which reacts more slowly, contributes only to the strength at a later stage. The reaction slowly continues producing calcium and hydroxide ions until the system becomes saturated and calcium hydroxide starts to crystallize. Simultaneously, calcium silicate hydrate begins to form. Tricalcium aluminate and tetracalcium aluminoferrite also react with water. Their hydration chemistry is more complicated as they involve reactions with the gypsum as well. Some of the hydration products contain nanometer-sized pores so that the size range of interest for these materials is from nm to hundreds of  $\mu\text{m}$ . Due to these complexities, many unanswered questions remain in the science of cementitious materials.

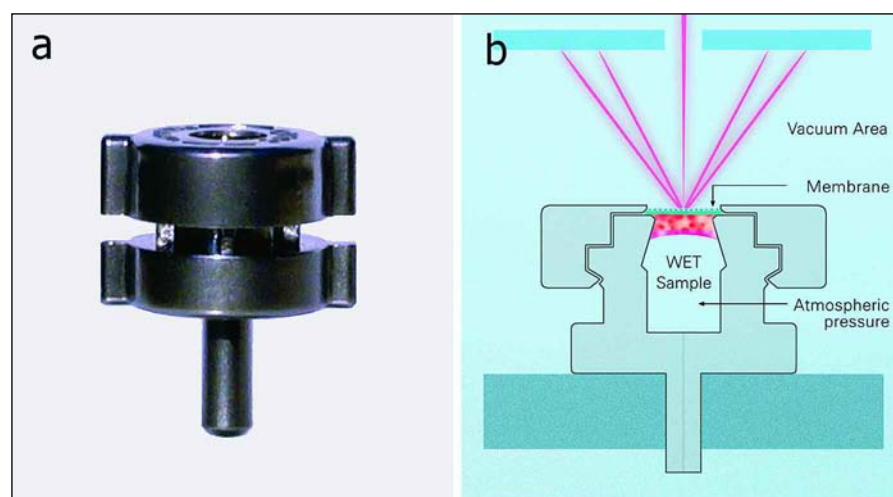


Figure 1:  
The capsule (a) and a schematic representation of the imaging process (b).

For cementitious materials, as for most materials of industrial interest, the key relationships between processing, microstructure and properties must be understood in order to have better control over the material in use. Development of new techniques for the characterization of cement is an important step to a better understanding of the hydration process in general and the effect of admixtures on that process in particular.

In this article we present results of in-situ studies done using a new wet-SEM capsule on Portland cement, gypsum and another commercial mixture, showing the potential of using this capsule to follow dynamic processes such as hydration.

## MATERIALS AND METHODS

### Cement specimens

All materials used in this study were commercial products and were purchased in a hardware store. Portland cement (Tambour) was mixed with tap water in a weight ratio of 0.35 (water/cement), gypsum powder (Nirlat) was mixed with tap water in a weight ratio of 0.7 (water/gypsum), and Maximo powder (Nirlat) was mixed with tap water in a weight ratio of 0.8 (water/binder).

### Scanning electron microscopy

All pastes were manually mixed and then immediately inserted into a WETSEM capsule (QuantomiX Ltd, Rehovot, Israel), sealed and mounted onto the microscope stage. The three in-situ experiments were conducted inside an FEI XL-30 scanning electron microscope operating in high-vacuum mode at 30 kV and equipped with an EDAX energy-dispersive X-ray spectroscopy detector. A solid-state backscattered electron detector was used to acquire the images. The hydration reactions were followed, and images were taken at different stages of the hydration processes. All three pastes were kept inside the closed capsule until the process had ended or slowed down dramatically. Therefore, levels of specimen hydration were maintained.

## RESULTS AND DISCUSSION

The wet-SEM capsule contains a thin polymer membrane which is transparent to electrons. The primary beam penetrates the membrane

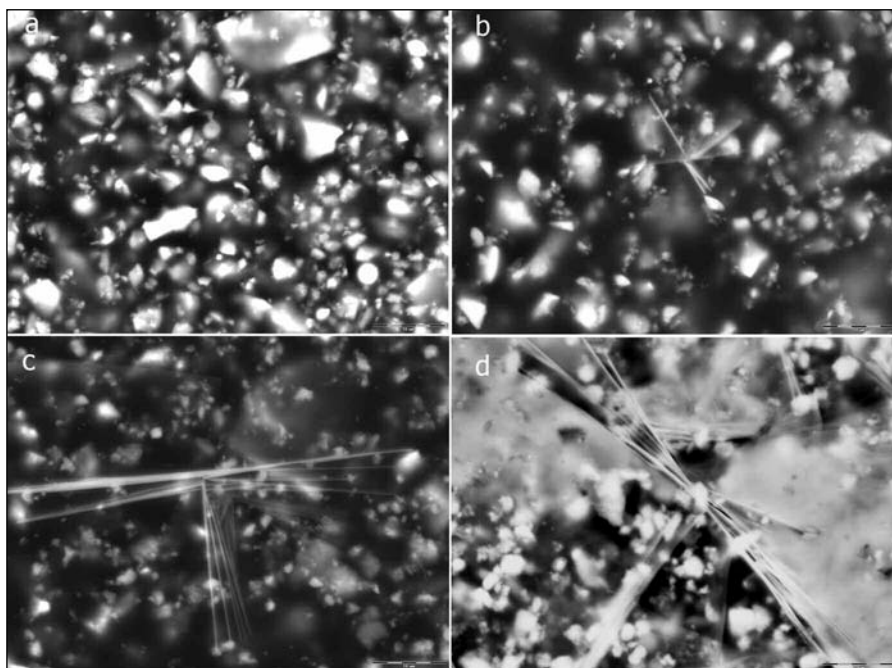


Figure 2: Backscattered electron micrographs of Portland cement (0.35 water/cement ratio) at early stages of the hydration process: 15 min (a), 3 hr (b), 7 hr (c) and 24 hr (d) after the powder was mixed with water. Scale bars = 10  $\mu\text{m}$ .

and after interacting with the sample the electrons have to escape through the membrane again in order to reach the detector. Since only the backscattered electrons have sufficient energy to escape through the membrane, the imaging is done using the backscattered electron detector. All images were acquired using the backscattered electron detector.

Figure 2 shows wet ordinary Portland cement at the early stages of the hydration process. The images in Figure 2a-d were taken at 15 minutes, 3 hours, 7 hours and 24 hours after the powder was mixed with water. The sequence of micrographs enables to follow the development of the reaction. In Figure 2a, taken 15 minutes after the initial mixing, the mixture is still in its original state and the unreacted particles can be seen. After the third hour (Figure 2b-d) hydration products can be seen to develop. After 24 hours (Figure 2d) calcium hydroxide crystals are seen to develop and cover large areas of the capsule membrane. From this point the hydration process of cement continues at a slower rate. If desired, the sample can be taken out of the

SEM and re-imaged even a few days or weeks after the reaction has started.

The penetration depth of the electron beam is up to approximately 3  $\mu\text{m}$  (depending on the acceleration voltage). Hence, the technology enables the imaging of only those parts of the particles that are within this depth. In Figure 2a some large particles can be observed, however only the edge of the particles can be clearly seen. For this reason, the method is not suitable for particle size distribution measurements. However, changes in the morphology can be observed very clearly.

Figure 3 demonstrates the possibility of imaging the reaction paste at higher magnifications where smaller changes can be observed. In the image, needle like particles, products of the cement hydration, are clearly seen growing out of the cement grains.

The capsule membrane is also transparent to X-rays, enabling the use of EDS analysis on the hydrating grains. Figure 4 shows an EDS spectrum of Portland cement (seen in Figure 2a), at the beginning of the hydration process. The contribution of the membrane to the



Figure 3: BSE image showing needle-like hydration products of Portland cement. Scale bar = 2  $\mu\text{m}$ .

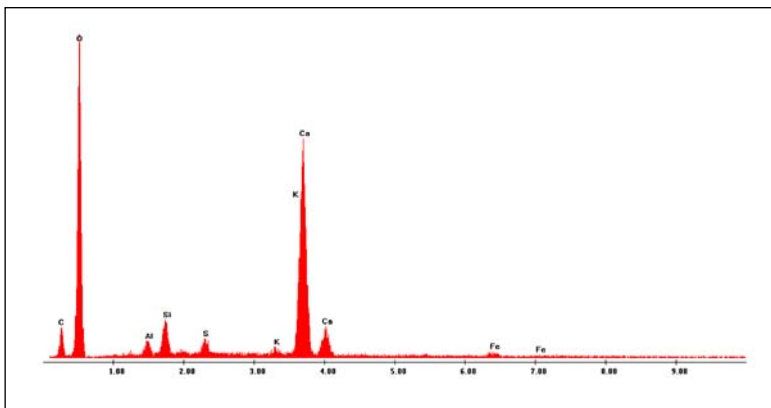


Figure 4: EDX spectrum of Portland cement obtained from area shown in Figure 2a at the beginning of the hydration process.

spectrum is the small carbon peak. All other peaks – O, Al, Si, S, K, Ca and Fe – were generated from the cement sample.

Figure 5 shows a sequence of four micrographs of gypsum taken 10, 20, 30 and 40 minutes after mixing with water. At 10 minutes (Figure 5a) unreacted grains can be seen dispersed in water with few needle-like crystals, whose growth can be followed in the micrographs taken at later stage (Figure 5b-d). The growth of needle like crystals can be followed with time and the formation of a network of gypsum crystals is evident within the first hour of observation. Figure 6 shows the same mixture after an hour, at a lower magnification, where the network of gypsum crystals is nicely observed.

In-situ observation of the hydration reaction of a commercial binder (Maximo, Nirlat) was started 13 minutes after mixing (Figure 7a). The images in Figure 7b-d were taken after 75 minute, 95 minutes and two hours after mixing. At 60 minutes almost no change in the morphology of the microstructure could be observed. Only after this induction period the reaction began and changes started to be observed as seen in Figure 7b. New crystals then started to form and their growth could be followed (Figure 7c) until a network of crystals was built, as seen in Figure 7d.

## CONCLUSIONS

Using the new wet-SEM capsules, specially designed for prolonged studies, the hydration reactions of three different binder mixtures have been followed inside a scanning electron microscope. The vacuum-tight capsules were kept closed throughout the studies, ensuring a constant water to binder ratio. In the three different systems the changes in the microstructures were observed and the growth of new crystals and creation of a cured network were followed over time. This new technology opens new possibilities in the research and development of cementitious systems and admixtures. The combination of in-situ imaging and material analysis makes it even more advantageous for the characterization and study of this kind of material.

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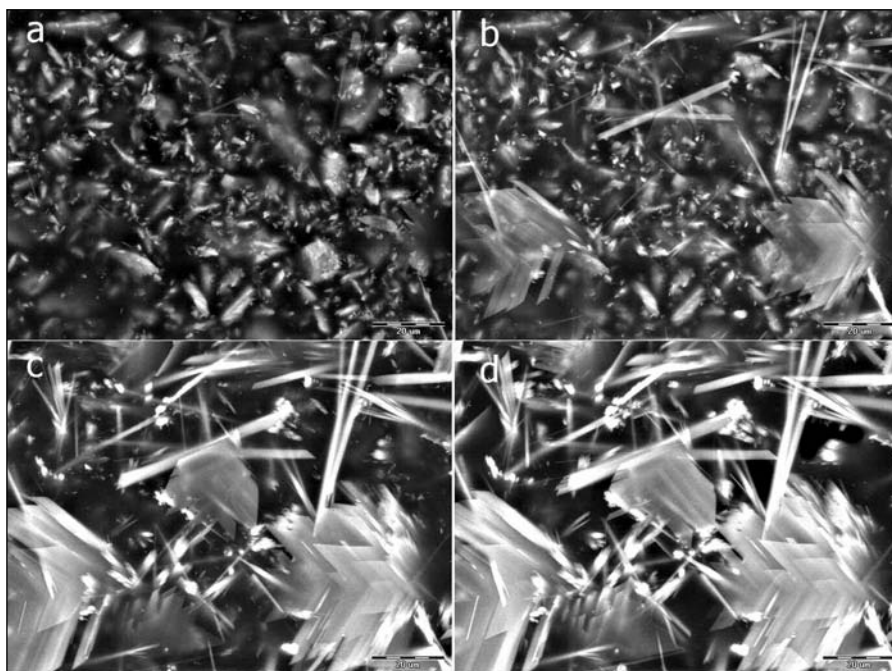


Figure 5: BSE micrographs of 0.7 water/binder ratio gypsum taken 10 min (a), 20 min (b), 30 min (c) and 40 min (d) after mixing with water. Scale bars = 20  $\mu\text{m}$ .

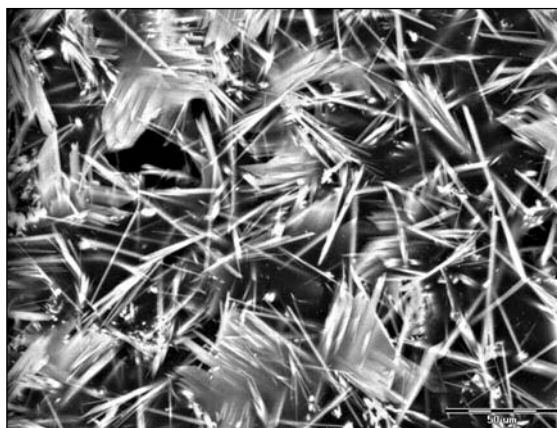


Figure 6: BSE image of gypsum (0.7 water/binder ratio) 60 minutes after mixing. A network of gypsum crystals is clearly observed. Scale bar = 50  $\mu\text{m}$ .

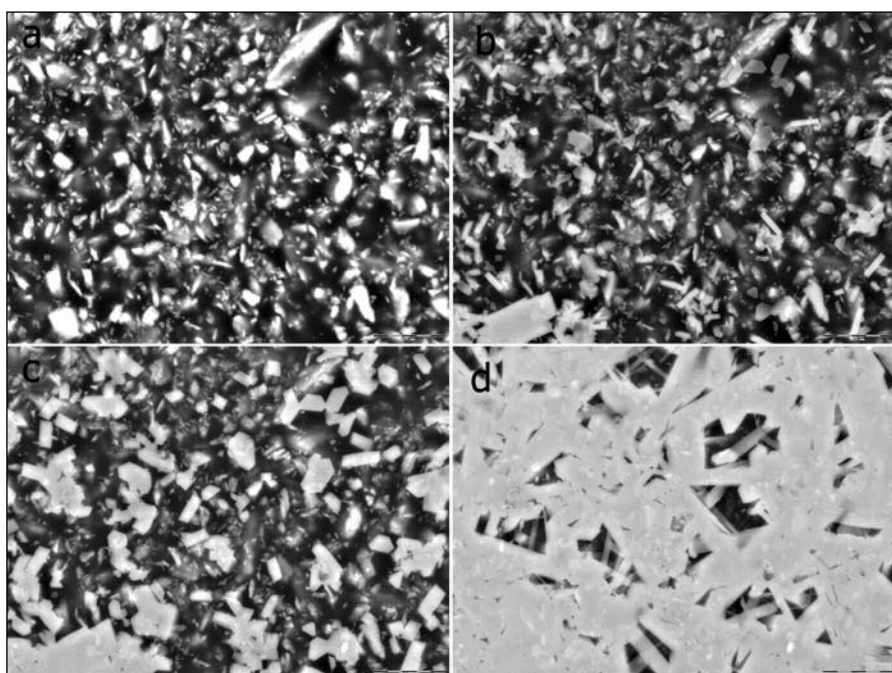


Figure 7: BSE images of commercial binder (Maximo, Nirlat) 13 min (a), 75 min (b), 95 min (c) and two hours (d) after mixing with water. Scale bars = 20  $\mu\text{m}$ .