Multiscale characterization of plaster setting using operando multiscale liquid-phase Electron Microscopies

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Background incl. aims
Gypsum has been traditionally used as a building material, but can also be a model for the development of injectable biomaterials for bone substitution. Set plaster, or gypsum ($CaSO_4.2H_2O$), is prepared by mixing dry hemihydrate powder ($CaSO_4.0.5H_2O$) with water. Its properties as a solid binder are largely influenced by the setting reaction occurring when $CaSO_4.0.5H_2O$ dissolve and crystals of gypsum precipitate. It is well known that the resulting solid is formed by an interlocked network of gypsum needles and platelets, but the exact setting process is not well understood yet. The objective of our study is therefore to monitor the evolution of crystals and understand the entire setting process, using operando observations [1], using Liquid-phase scanning electron microscopy.

Methods
For Scanning Electron Microscopy (SEM) experiments, the hemihydrate powder is manually mixed with an aqueous solution containing 5.2 mM citric acid. Plaster paste is then deposited onto the window of a Quantomix cell placed in a Zeiss Supra 55VP SEM microscope. Such cells are indeed water - and airtight, and therefore plaster evolves under the same conditions as in real use, especially in terms of water-to-plaster ratio. Gypsum crystallization is followed by taking SE and BSE images every 30 s.

In situ Environmental Transmission Electron Microscopy (ETEM) experiments are performed on a Titan ETEM from FEI/TFS. The hemihydrate powder is dry deposited onto a grid covered with a holey carbon membrane, then placed on a cryo-holder from Gatan/Ametek. The temperature is slowly decreased to 0°C and once stabilized, the partial pressure of H_2O is increased until liquid water covers the hemihydrate particles.

Results
The dissolution of hemihydrates and crystallization of gypsum is followed operando in SEM. Image processing and analysis procedures are developed to segment the gypsum crystals and follow their growth vs time. Based on geometric information and the knowledge of the equilibrium morphologies [2], we propose an indexation of the crystal facets (see example in Figure 1). The growth rates of the different planes, including unstable ones, is measured.

In situ experiments in ETEM give a more precise view of the onset of gypsum nucleation, with the formation and evolution of facets at the nanometer scale.

Conclusion

The use of liquid-phase electron microscopy at different scales allows the investigation of gypsum growth in a real plaster mixture. The formation of unstable facets and their transformation into stable ones are evidenced from the onset to full plaster setting. Moreover, the growth rates for all types of facets can be measured and compared with the few values found in the literature. The influence of several parameters is discussed (addition of a retardant, presence of a membrane, image acquisition conditions and irradiation damage) [3].

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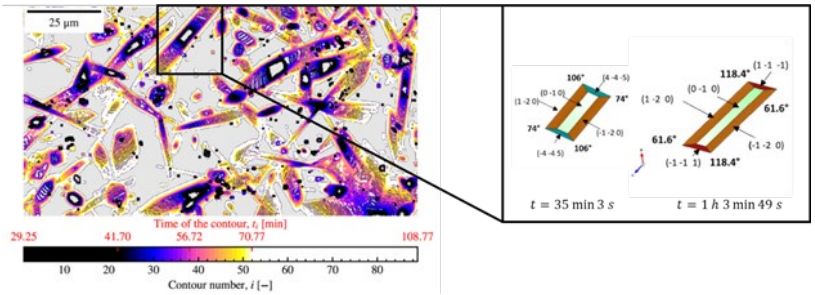
Figure caption

Growth of the gypsum crystals during plaster setting and indexation of a crystal for two different times.

Graphic:



Keywords:

operando, liquid, crystal, growth

Reference:

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