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In Situ Observation of Hydrating Cement-Clinker-Phases by Means of Confocal Scanning Microscopy - First Results

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IN SITU OBSERVATION OF HYDRATING CEMENT-CLINKER-PHASES BY MEANS OF CONFOCAL SCANNING MICROSCOPY – FIRST RESULTS

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ABSTRACT

Many previous investigations have been conducted on the hydration of cement.

This work presents a new method for pursuing the hydration of cement with confocal scanning microscope techniques (CSM).

The hydration of pure cement clinker phases were observed after the addition of either calcium sulfate solution or pure water. In the case of the aluminates ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) hydration in the presence of sulfate two phases of crystallization were observed:

- A first rapid growth of a layer covering aluminate grains with long needle like crystallites
- A second, slower growth of a inner layer existing of smaller crystallites

A new perspective for a better understanding of the crystallization and changes in micro- and mesostructure of cement based materials is given.

INTRODUCTION

Nowadays researchers have a lot of methods to investigate the hydration of inorganic binding materials. Although most of them can not use for in-situ observations.

The uninterrupted observation of crystal growth for Calcium Silicate Hydrates (CSH) or Calcium Aluminum Hydrates (CAH) is most often performed using Environmental Scanning Electron Microscopy (ESEM).

The ESEM method stipulates a low pressure of 0.1 - 10 Torr. These conditions could be determinantal to test results because they deviate from standard atmospheric conditions.

Optical microscopy enables the sample to be observed up to a magnification of 1000x, without the preparation relicts and the measurement influencing the sample. At the moment the observation of sporadic distributed clinker particles is possible.

This work gives an insight into the state of the art in-situ-measurements of the system $3\text{CaO} \cdot \text{Al}_2\text{O}_3 - \text{Ca}(\text{OH})_2 - \text{CaSO}_4 - \text{H}_2\text{O}$.

EXPERIMENTAL

Equipment

Microscope

An inverted microscope with a confocal scanning unit (Nikon TE300 inverted microscope with a Nikon PCM 2000 confocal unit) is used to illuminate and observe samples (figure 1). The confocal principle is a well known technique in biology [1].

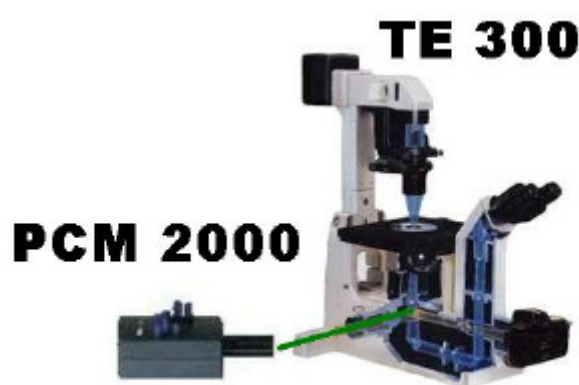


figure 1: Inverted Microscope (TE 300) and confocal scanning unit (PCM 2000)

The advantages of this technique are the high resolution of the images and the possibility of the three dimensional image reconstruction. Confocal microscopy means that the objective lens is used both to illuminate the sample and to observe it. Illumination is achieved by lighting through a pinhole such that the sample becomes a source of light. A second pinhole enables an optical examination of individual planes of the sample. As the sample is scanned the three dimensional image is built up pixel by pixel. The reemitted light from the specimen can contain various information about the sample dependant on the mode of observation. Sample topography can be analyzed from the reflected light. The image contrast can be improved by using a fluorescent dye and observation of the fluorescence. Through analyzing the non elastic scattered excitation light, the Raman light, information about the distribution of chemical compounds can be determined. This is made possible by the Confocal Raman Microscope (CRM) shown in figure 2 (set-up of the University Bayreuth /2/).

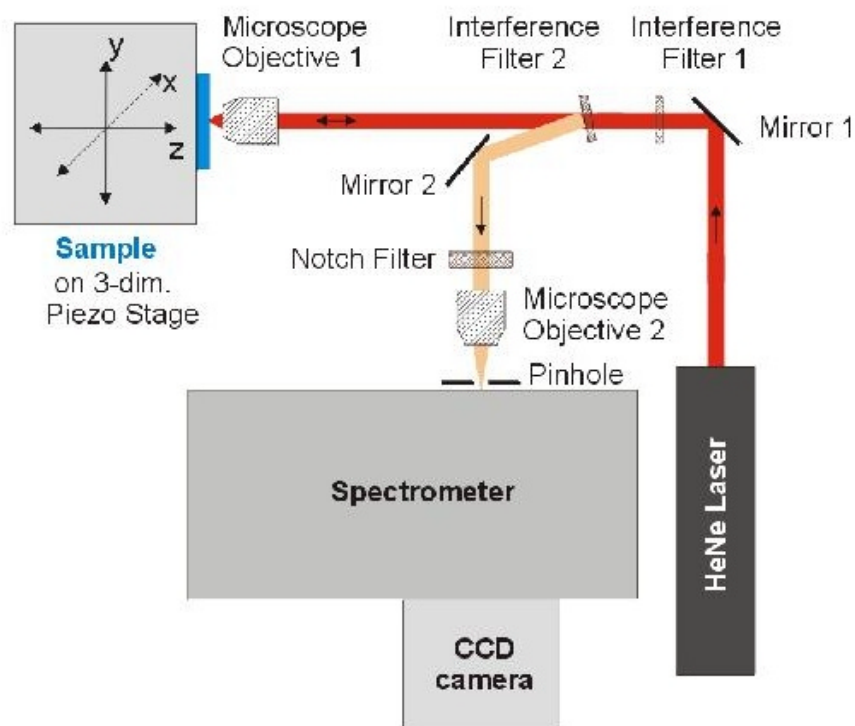


figure 2: Optical set-up of the Confocal Raman Microscope

Calorimeter

Calorimetric investigations render the heat evolution of chemical reactions.

The isothermal calorimeter TONICAL (TONI TECHNIK) was used at 20°C. In this case the hydration of C_3A was studied influenced by different solved ions. Preparation consisted of 5 g C_3A in a test tube, 2.5 g of water or solution in a syringe with a canula which were put in the calorimeter over night, to get thermal equilibration.

Materials

The Dye Rhodamine B

An increase in image contrast was attain by using a dilute Rhodamine B dye from Radiant Dyes (figure 3). The excitation wavelength was 543 nm and the fluorescence was observed above 560 nm.

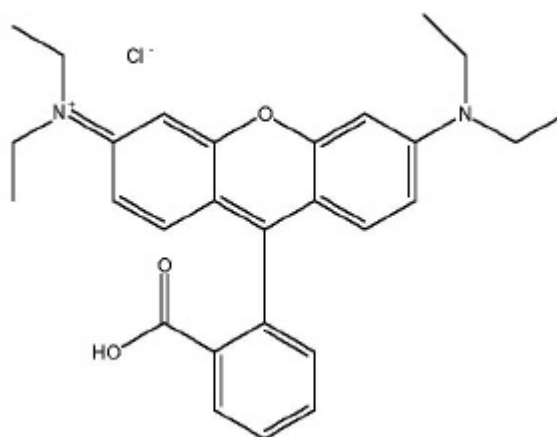


figure 3: Chemical structure of Rhodamine B /3/

Calcium aluminate

Calcium aluminate was produced by burning homogenized stoichiometric mixture of calcium carbonate and aluminum oxide (Merck) at 1450°C for 15 h. The Clinker was ground to 3100 cm² according to BLAINE.

Aqueous Solutions

Deionized water was shaken with an excess of gypsum or calcium hydroxide for 1 h and filtered. By this way the saturated solutions were obtained. Then a small amount of Rhodamine B ($c < 10^{-3}$ mol/l) was added.

Sample Preparation for CSM

Some C_3A was put on a slide and water or a solution was added. Long-term investigations use a cover-glass to enclose the sample on the slide. The cover-glass is then glued in place on the slide (figure 4).

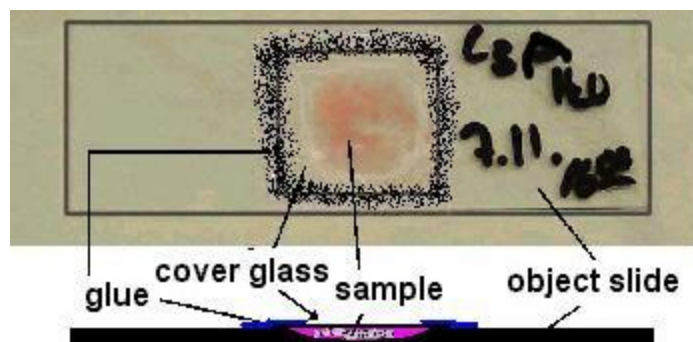


figure 4: Preparation for the CSM

RESULTS AND DISCUSSION

Calorimetry

As mentioned above fluorescent dye Rhodamine B was added to the reaction water. The dye does not influence the hydration kinetics of C_3A (figure 5).

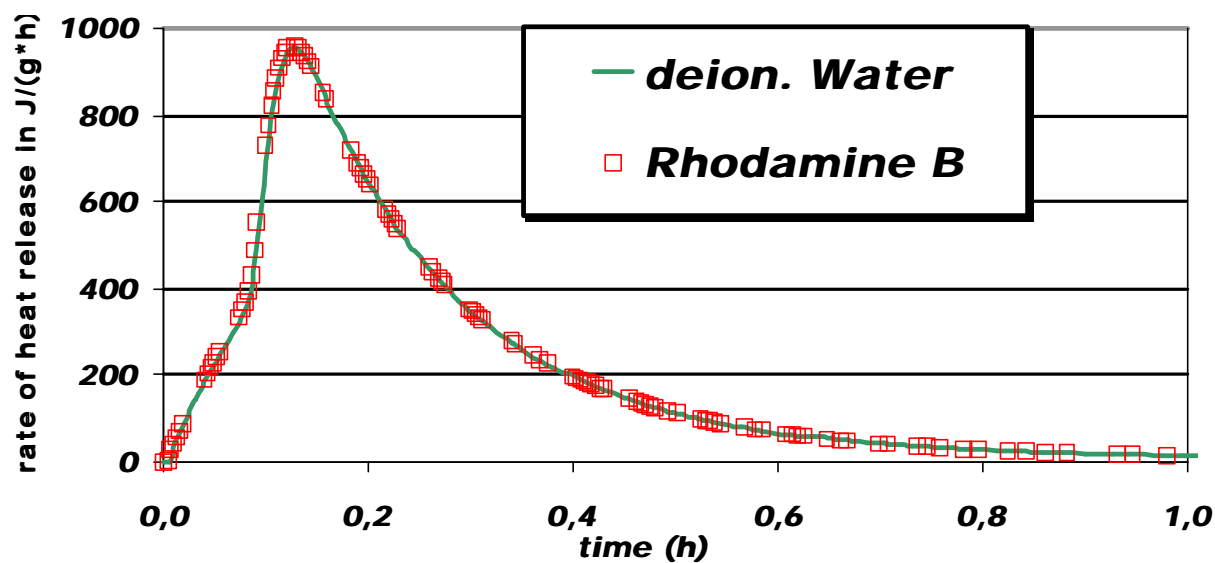


figure 5: Calorimetric measurements of C₃A hydration with and without Rhodamine B in the added water

With solved calcium hydroxide the heat evolution was almost the same in comparison with pure water. This maximum occurred later when gypsum solution was used.

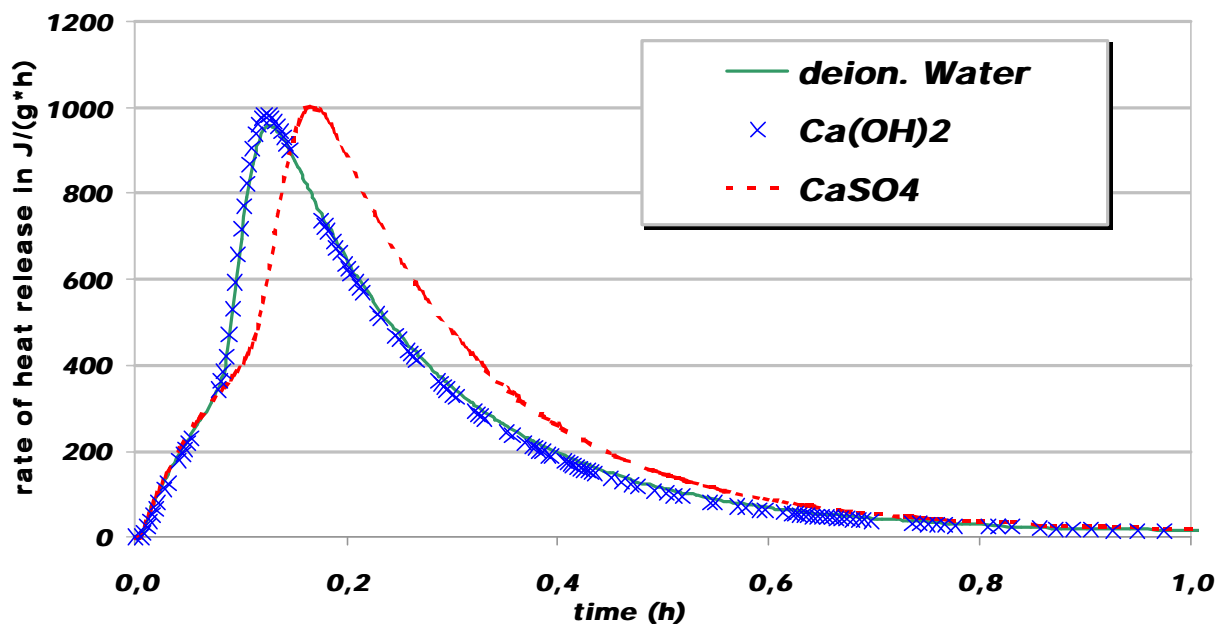


figure 6: Heat release of C₃A hydration with different solved ions

Confocal Scanning Microscopy (CSM)

System 1: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-CaSO}_4\text{-H}_2\text{O}$

The very first results were obtained by observing coarse C_3A particles reacting with saturated gypsum solution. This experiment was executed in a scanning mode but the sample was illuminated using a phase contrast aperture.

Figure 7 shows

- A first rapid growth of a layer covering aluminate grains with long needle like crystallites (within 50 minutes)
- A second, slower growth of a inner layer existing of smaller crystallites (after 2 hours)

The crystallites were very big, because of the extreme high w/c ratio the crystallization was not hindered by other particles.

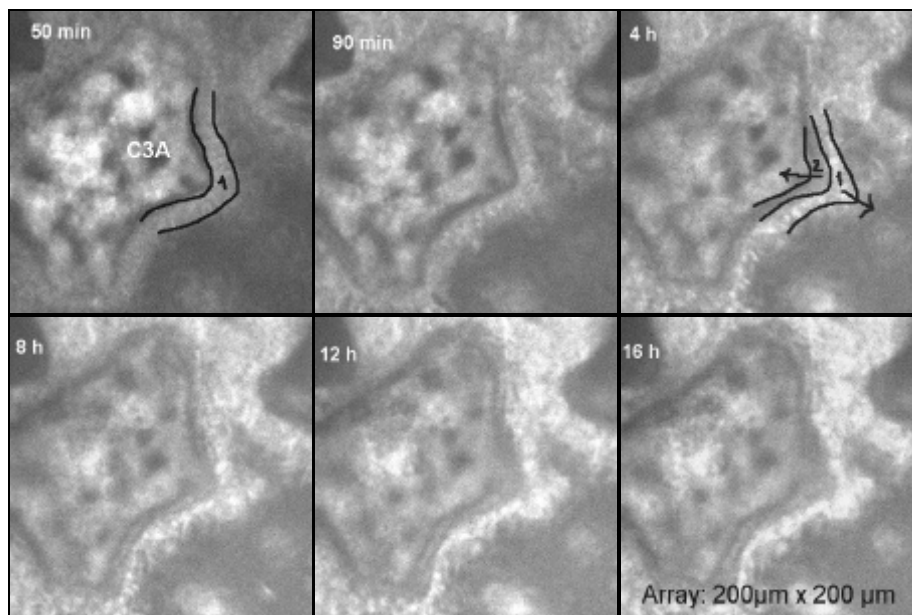


figure 7: C_3A reaction with saturated gypsum solution; the two layers and their growth direction are marked

The images given in figure 7 do not contain any information about the composition of the solids or liquids. Therefore, in addition the composition was analyzed using a Confocal Raman Microscope.

The aim of this experiment was to record the Raman line intensity of ettringite at 995 cm^{-1} /4/ in two dimensions. Results for the Raman analysis gave lines of very low intensity (no figure shown). They also seem to be just statistical distributed.

Possible reasons are:

- There was insufficient sulfate in the solution
- New formed phases have a poor grade of crystallization

Even if the case that a solid mixture of C_3A and gypsum (1:1 molar) had reacted with water, no ettringite was measured as a result. But within the smaller lines of the Raman spectra indicating the presence of gypsum or C_3A (only at 762 cm^{-1}) an intensive Sulfate Raman line (ν_1) occurs at 1013 cm^{-1} (figure 8).

The Rayleigh line is a result of the elastic scattered excitation light. The intensity distribution of the Rayleigh line maps the topography of the sample, whereas the Raman signals yield information about the spatial distributions of the corresponding chemical species.

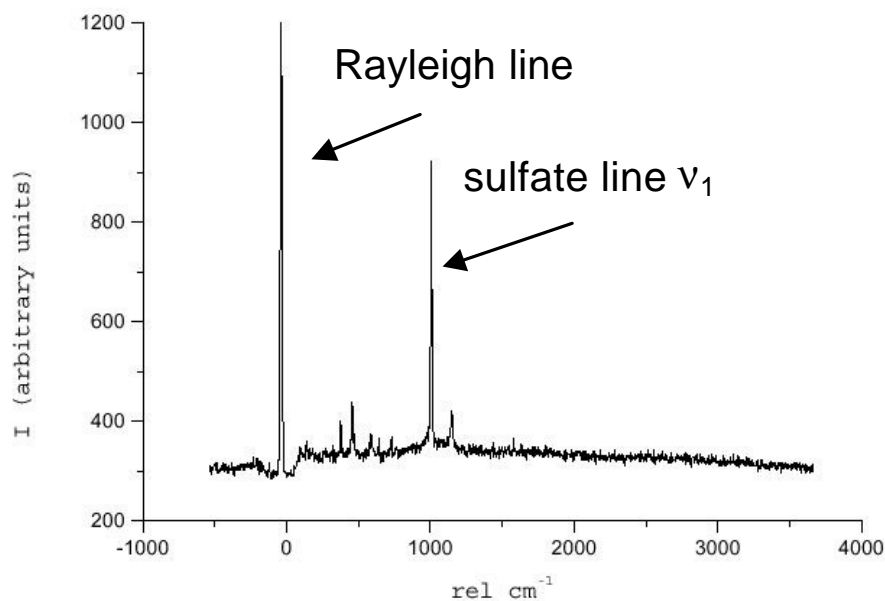


figure 8: typical Raman spectrum of sample C_3A + gypsum + water

Because of this it was possible to scan an array of $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ to investigate the gypsum distribution (figure 9).

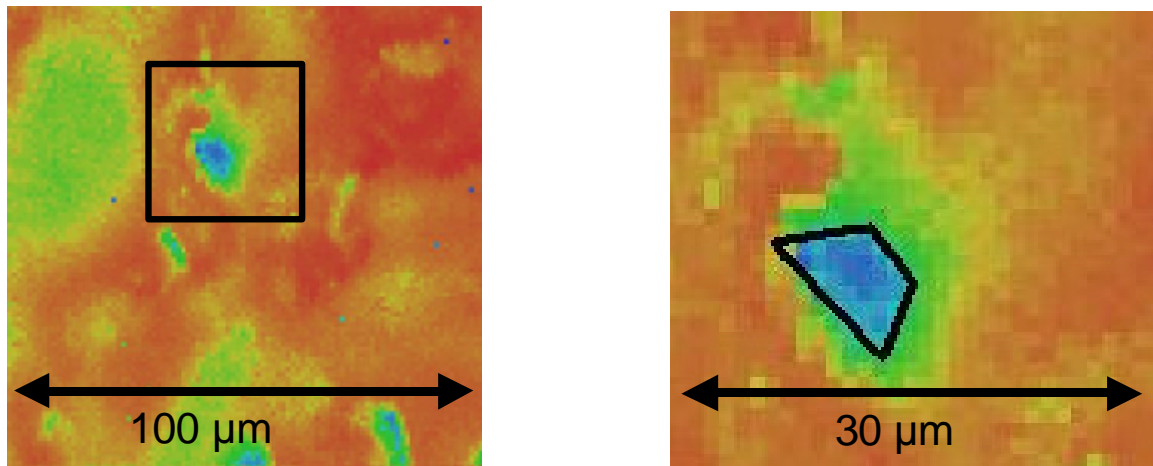


figure 9: Raman image of a C_3A /gypsum paste at 1013 cm^{-1} , right: zoomed clipping, of the marked area; intensity increases from red over green to blue

Figure 9 shows that an analysis of different gypsum compositions is possible. A three dimensional resolution is also possible, but not shown here. In the zoomed image of figure 9 (right) a trapezoidal structure is emphasized which can be interpreted as a gypsum crystallite.

System 2: $3CaO \cdot Al_2O_3 - Ca(OH)_2 - H_2O$

For this experiment saturated calcium hydroxide solution with Rhodamine B was used (figure 10). In comparison with figure 7 the resolution was much better, although a higher magnification was applied. The series of images in figure 10 shows, that CAH crystallizes directly in the spaces between the clinker particles (example areas are marked).

After one hour the new formed crystallites cover the C_3A particles completely. The morphology of these phases differs in comparison with experiments carried out using saturated gypsum solution. However, in both cases the formation of new phases takes place after a 30 minute time interval.

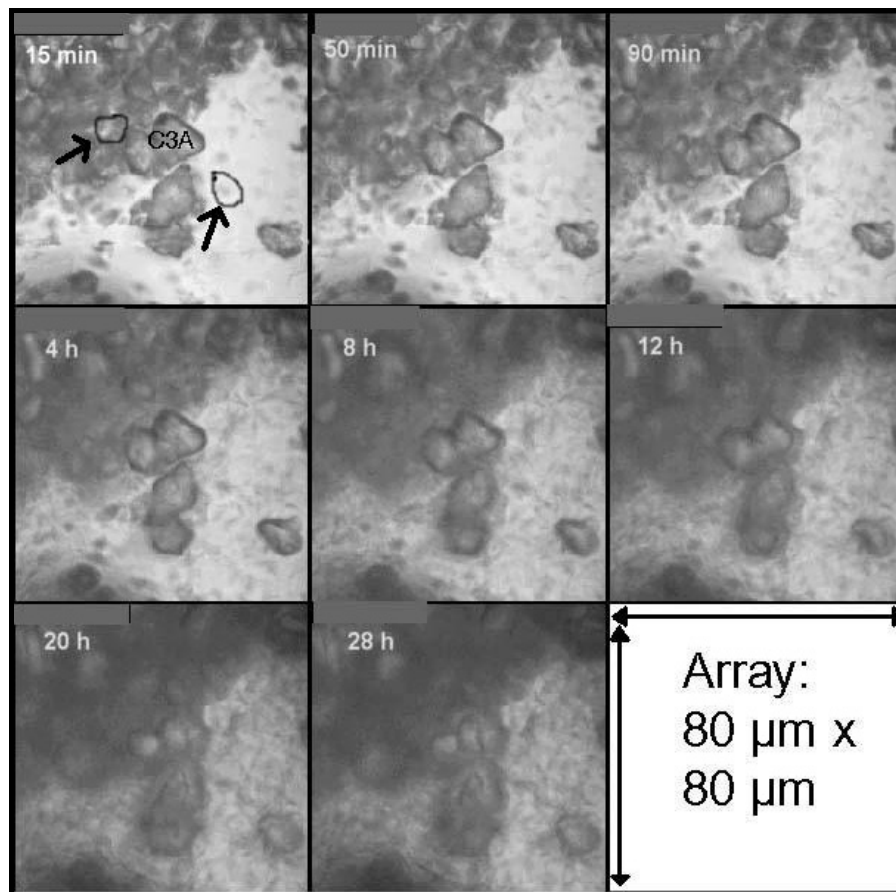


figure 10: Image series of hydrating C_3A with saturated calcium hydroxide solution (Rhodamine B added); for example marked areas: initial formed CAH crystallites

This agrees with the well known mechanism of C_3A hydration. In the presence of sulfate ettringite is formed rapidly. Although the initial crystallites are quite small (length: about 0.5 - 1 μm , diameter: 0.1 - 0.5 μm , see figure 11, left) and can not be visualized by the CSM. In the absence of sulfate hexagonal calcium aluminate hydrates are formed. They effect the fast stiffening of cement if no sulfate carrier is added. The CAH crystallites are big enough to be observed with the CSM.

The difference in heat release developed for C_3A with and without sulfate in the added solution as shown in figure 6 can also be identified in the kinetics of CA(s)H crystal growth.

CONCLUSIONS

In the publication the different applications of Confocal Scanning Microscopy (CSM) were presented.

The advantages of the CSM are the simple sample preparation and, in comparison with ESEM or SEM, the simple handling.

However the possible maximal resolution in CSM is much lower because it is limited to the wavelength of the light. The initial formation of CSH and CAH phases during cement hydration are very small (0.010 to 1 μm) and it is not possible to get images like the ESEM images taken from /5/ and /6/ (figure 11).

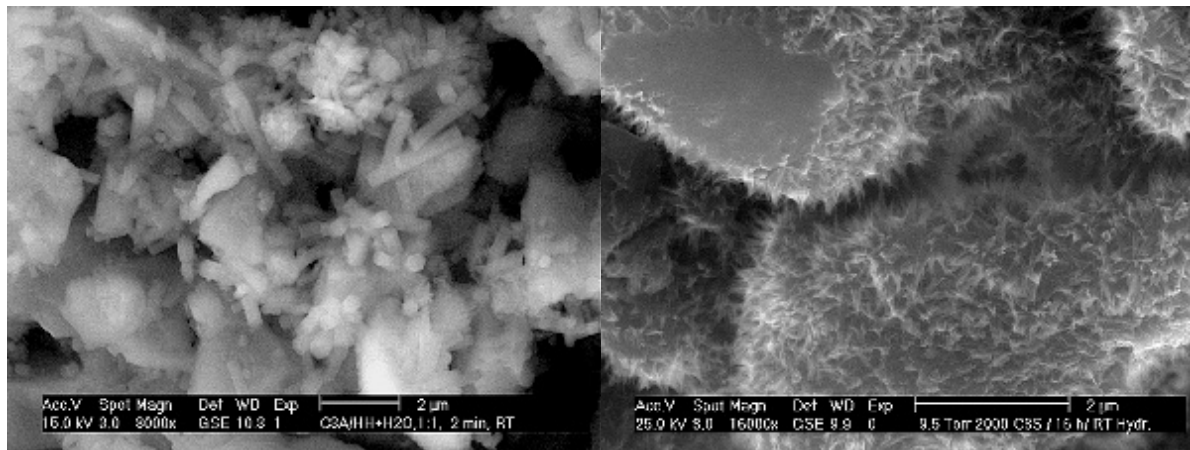


figure 11: ESEM images; left : C_3A -calcium sulfate hemihydrate mixture reaction time with water: 24 h; right: C_3S reaction time with water: 16 h (taken from /5/ and /6/)

In further investigations of cement hydration the method could be used to verify calculation of the crystal growth obtained by computer programs (for example 'cemhyd3d' /7/).

With the CSM it is possible to get a rapid three dimensional image of structures larger than 5 μm with numerous possible adaptations of the experimental conditions to represent a realistic environment.

Using the information of the Raman spectrum the possibility imaging different chemical compounds spatially resolved is given. This method works if the Raman lines of the investigated compounds are intensive enough and do not interfere.

The imaging method is limited to record surfaces for not transparent samples.

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