

The Phase Transformation of Calcium Sulphate Sub-hydrates Reacting with Water

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Abstract

In literature there exist some well-known theories about the phenomena taking place when calcium sulphate sub-hydrates react with water. The growing of gypsum crystals out of a supersaturated liquid was described by Le Chatelier in 1919.

Another kind of reaction was published by Perederji in 1956 and Eipeltauer in 1960. They described the crystallisation of gypsum as an inner reaction in the calcium sulphate sub-hydrates by an inner transformation of the crystal structure.

In literature however there has not been an experimental verification for the second theory so far. Therefore we have investigated the reaction of calcium sulphate sub-hydrates with water under optical microscopy. Therefore we have invented a special measurement cell. The results obtained by optical microscopy are supported by those obtained by other methods, i.e, heat flow calorimetry and scanning electron microscopy and correlate very well with each-other.

Thus we have been able to show that the mechanism of the reaction, which was described by Le Chatelier and that of the reaction published by Perederji and Eipeltauer are taking place parallelly. The results can be observed in short films and single pictures for α - and β -calcium sulphate sub-hydrates.

Introduction

The crystals which are described in literature are different in their morphological behaviour. There have been observed some kind of long, more or less branched-like crystal needles, flat twined crystals and small crystals without a macroscopic structure described. For the different crystal morphologies also different theories about the phenomena taking place by the reaction of calcium sulphate sub-hydrates reacting with water have been proposed.

One of the aims of this work is to show as much of these phenomena and as much of the crystal-morphologies as possible in a film of pictures taken by optical microscopy. To understand the difference between these reactions: special α - and β -calcium sulphate sub-hydrates, which were accelerated to a reaction time of fifteen minutes, were measured with other methods. The methods which were used are heat flow calorimetry, *in situ* x-ray-diffraction, sonic wave measurement and scanning electron microscopy. After these measurements some films of the hydration of industrial calcium sulphate sub-hydrate were taken to show the differences between the morphologies of the product-crystals. The measurement has also been done with the same calcium sulphate sub-hydrate with different sized crystals.

Experimental

First of all there was a try to take the film under the optical microscope with a simple test arrangement which was built of a slide with the sample and water on it covered by a glass plate on the top. The disadvantage of this arrangement is that the sample dries out after round about one hour. Therefore another arrangement has to be established. So a small rubber ring is glued with grease on the slide and closed in the same way by a glass plate. This measurement cell is shown in picture 1.



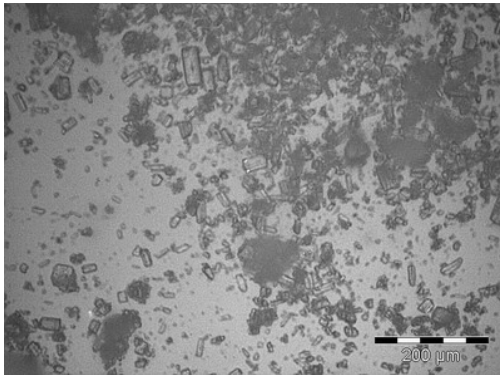
Picture 1 Measurement cell

If this new arrangement is not absolutely filled with water, some small drops will form on the glass plate and the pictures get unclear. To prevent this effect the measurement cell has to be filled completely with water. Because of this the water/gypsum ratio is kept to high. The effect of the water amount on the reaction was tested by the heat flow calorimetry and no effect could be proofed. This cell is closed for about one week; if a longer reacting time is needed, it is possible to use a two component resin instead of the commonly used fat as sealing component. The cell may be closed for more than one year, but it is not possible to use the rubber ring and the glasses again. After the addition of water every 60 seconds a picture was taken with 200 times magnification for about 3 hours.

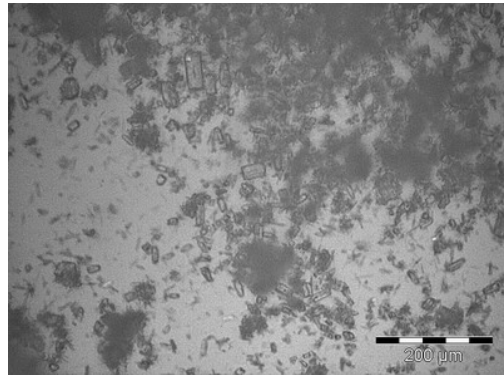
For the *in situ* x-ray diffraction the sample holder was filled with the Gypsum and scanned by the x-ray diffraction before starting the reaction. The sample was not grounded because the smaller calcium sulphate sub-hydrates react faster. After measuring the dry sample, the reacting water is given on the sample dropwise from a syringe and the measuring was started. In eighteen minutes fifteen diffraction patterns were taken. After the measurements the results were analysed with the Rietveld method. The samples were stored water- and airtight at 25°C.

Results

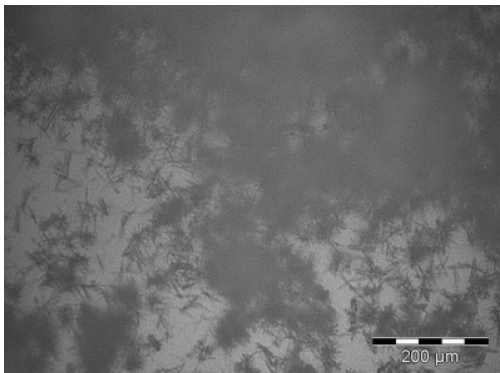
The sub-hydrate, which was accelerated to a hydration time of fifteen minutes, was first measured by optical microscopy in the described measurement cell. The results are shown in pictures 2-4 for the α -sub-hydrate and in pictures 5-7 for the β -sub-hydrate.



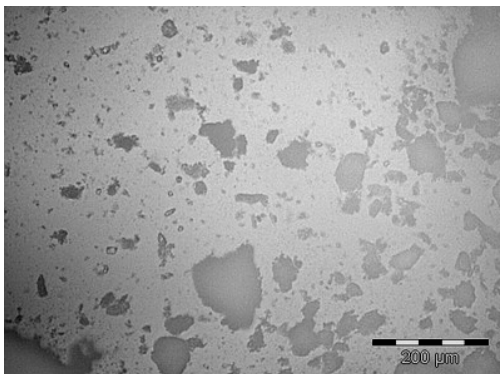
Picture 2 α -sub-hydrate 1 minute after addition of water



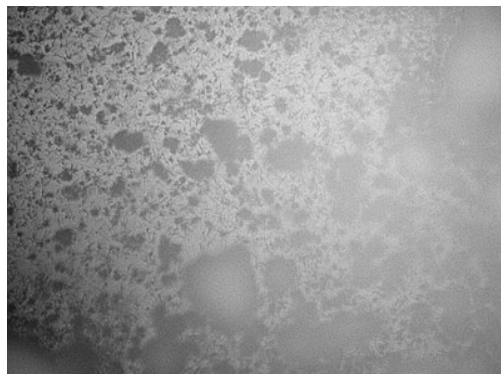
Picture 3 α -sub-hydrate 18 minutes after addition of water



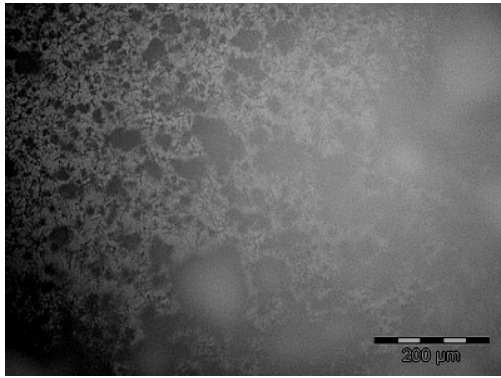
Picture 4 α -sub-hydrate 60 minutes after addition of water



Picture 5 β -sub-hydrate 1 minute after addition of water



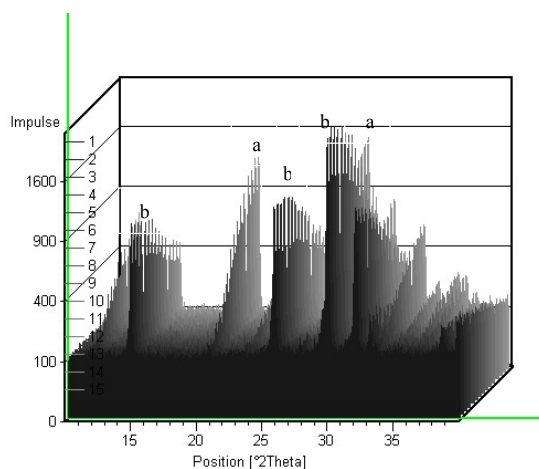
Picture 6 β -sub-hydrate 18 minutes after addition of water



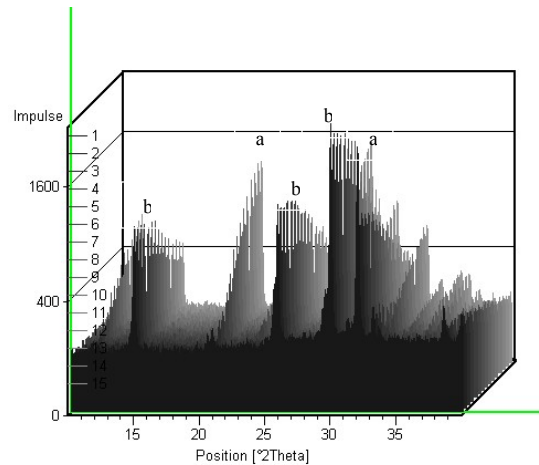
Picture 7 β -sub-hydrate 60 minutes after addition of water

These pictures show that the α -calcium sulphate sub-hydrates have larger crystals than the β -type and the α -crystal products are also larger. The dissolving of the sub-hydrates and the growth of the gypsum crystals from the liquid can be observed in both types of sub-hydrate.

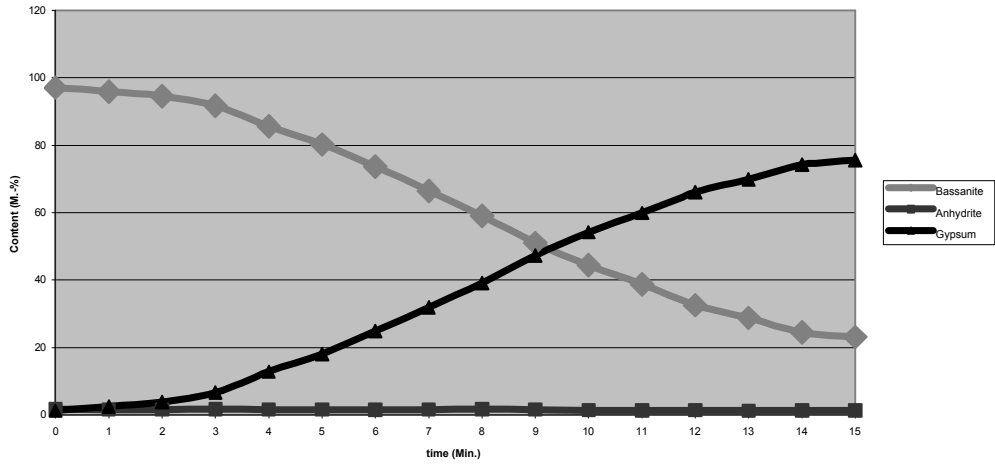
The results of the same sample measured by the *in situ* x-ray diffraction are shown in pictures 8 and 9, the peaks of the dihydrate are labelled with a, those of the subhydrate with b. The results from the Rietveld method are following in pictures 10 and 11. The pictures show that the amount of sub-hydrate is getting less and the amount of gypsum is growing. The anhydrite can be used as an internal standard to see how the growth of the gypsum crystals influences the measurement.



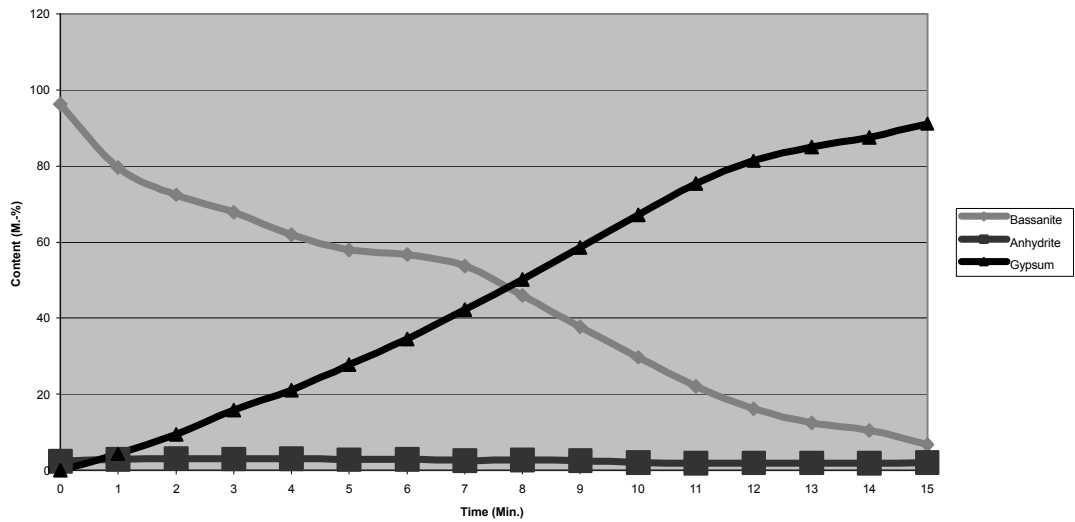
Picture 8 *in situ* XRD accelerated α -sub-hydrate hydration-time 18 minutes



Picture 9 XRD accelerated β -sub-hydrate hydration-time 18 minutes

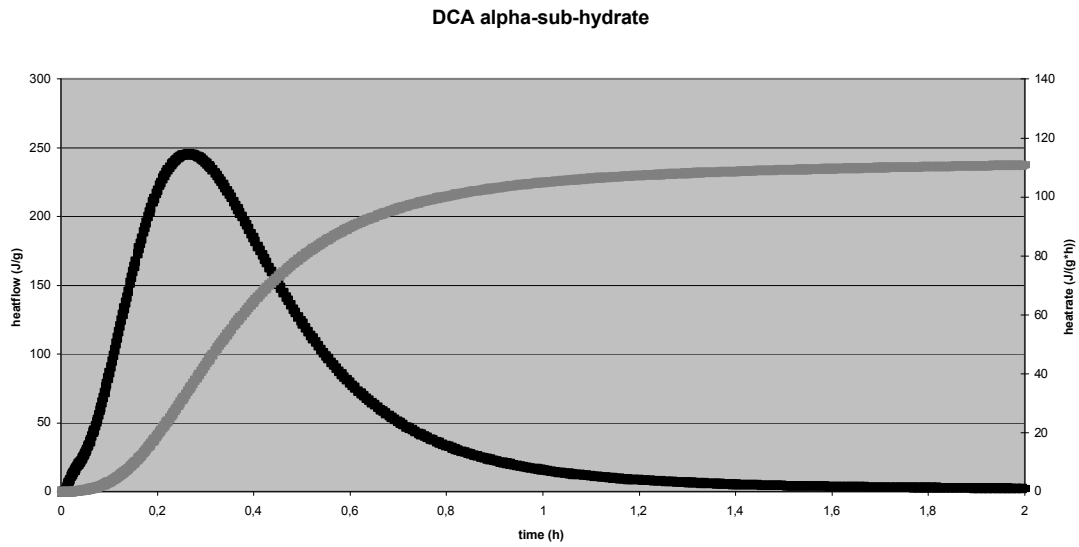


Picture 10 Rietveld results α -sub-hydrate accelerated hydration-time 18 minutes

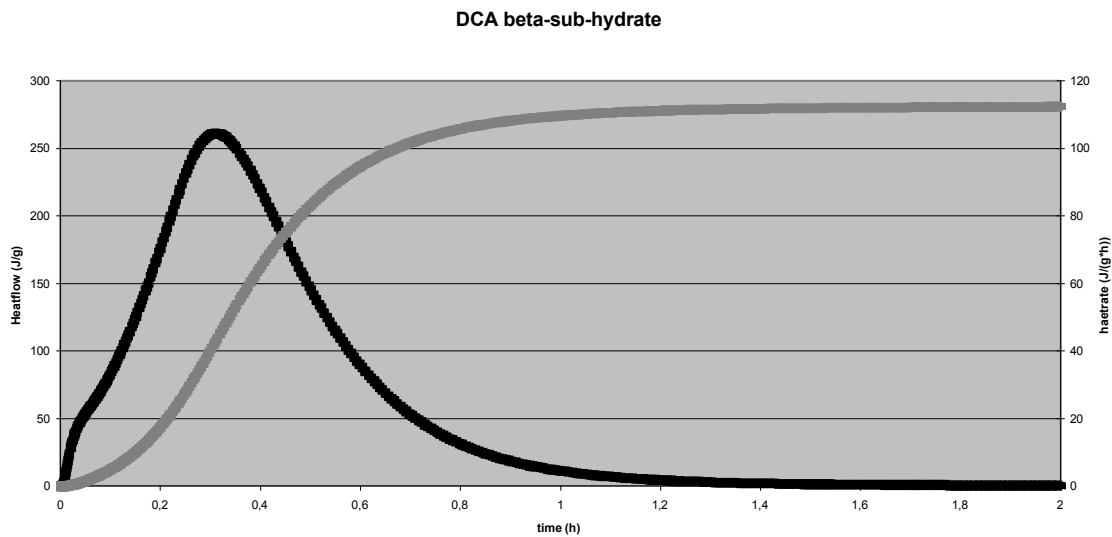


Picture 11 Rietveld results β -sub-hydrate accelerated hydration-time 18 minutes

The same sub-hydrate was measured by the heat flow calorimetry and the results are shown in pictures 12 and 13.

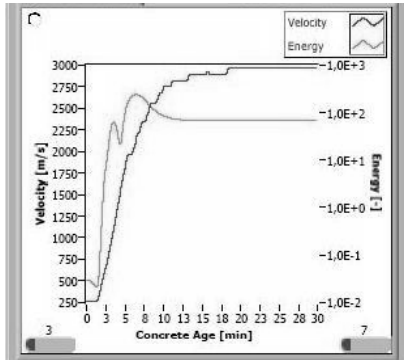


Picture 12 Heat flow calorimetry α -sub-hydrate accelerated hydration-time 18 minutes

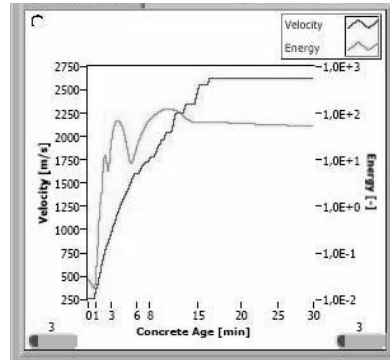


Picture 13 Heat flow calorimetry β -sub-hydrate accelerated hydration-time 18 minutes

The same samples were measured by sonic wave measurement and the pictures 14 and 15 show the results.



Picture 14 Sonic wave results
 α -sub-hydrate

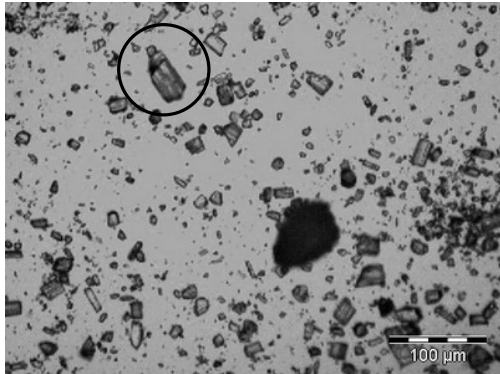


Picture 15 Sonic wave results
 β -sub-hydrate

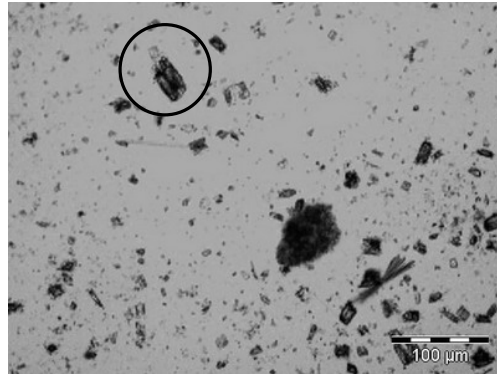
The sonic wave measurement is used to characterise the crystallisation of the gypsum. The consolidation starts after one minute and ends at round about 16 minutes. This fact can be detected by an increase of the sonic wave energy. It is an alternative method for the Vicat-test which is described in DIN 196-3.

The heat flow calorimetry shows that the reaction stops after round about one hour. So it is shown that the gypsum is reacting after the end of the consolidation. It is useful to take pictures for the film with the optical microscope for one hour or more.

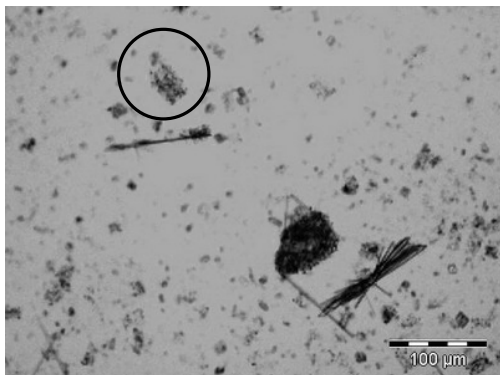
After these measurements other gypsums were measured by optical microscopy. By these measurements it was possible to investigate different types of hydration. The sub-hydrate gets dissolved in the water and new gypsum crystals are growing. Parallel to this mechanism, an inner hydration has been investigated. Pictures 16 to 18 show this.



Picture 16: α -sub-hydrate after 1 minute



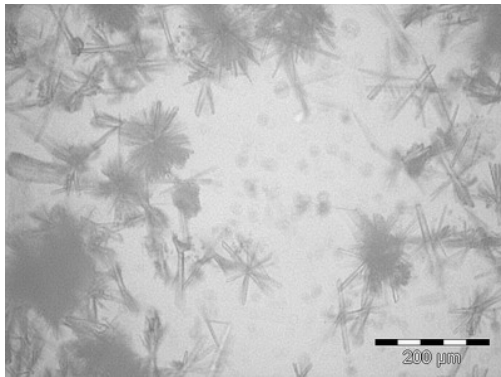
Picture 17: α -sub-hydrate after 90 minutes



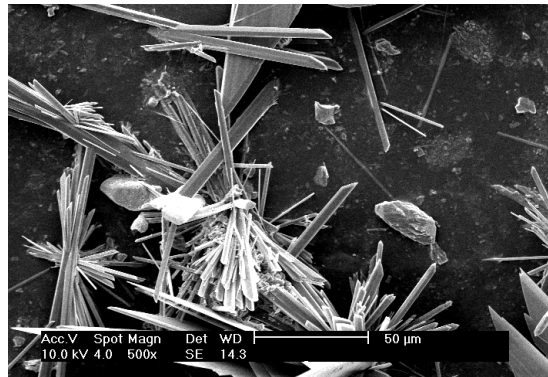
Picture 18 α -sub-hydrate after 180 minutes

The crystal which shows the inner hydration is marked by the circle.

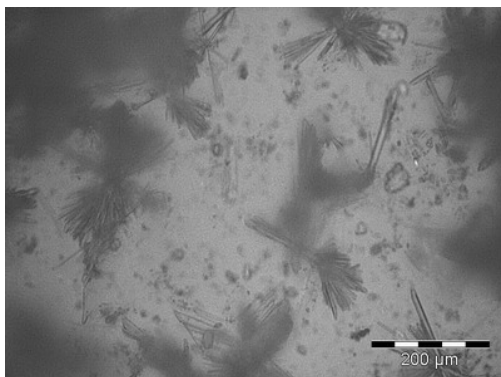
By observing different industrial gypsums with means of optical microscopy different crystal morphology was investigated. These differences are shown by optical microscopy and scanning electron microscopy in pictures 19-24



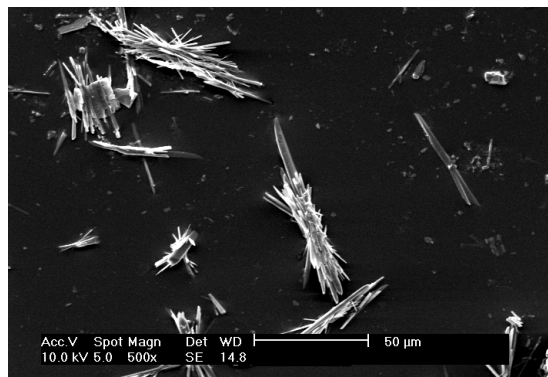
Picture 19 Technical gypsum1 after 4h in water picture taken by optical microscopy



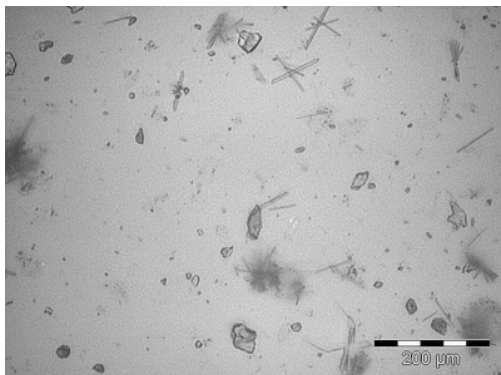
Picture 20 Technical gypsum1 after 4h in water picture taken by SEM



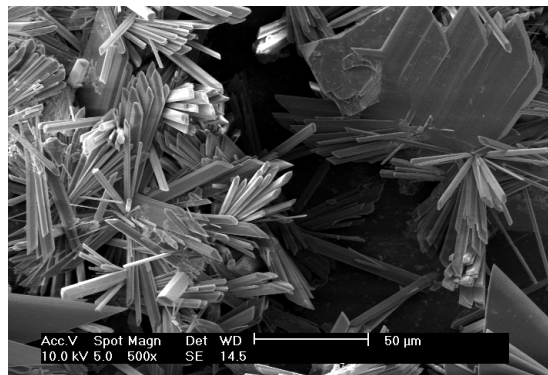
Picture 21 Technical gypsum2 after 4h in water picture taken by optical microscopy



Picture 22 Technical gypsum2 after 4h in water picture taken by SEM

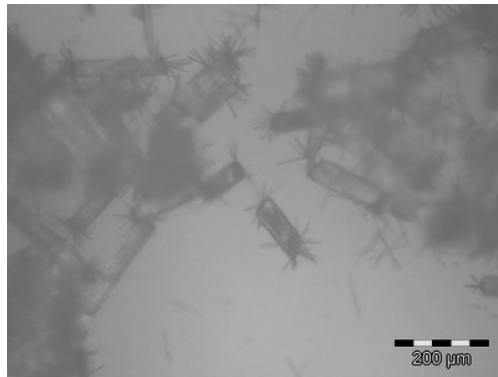
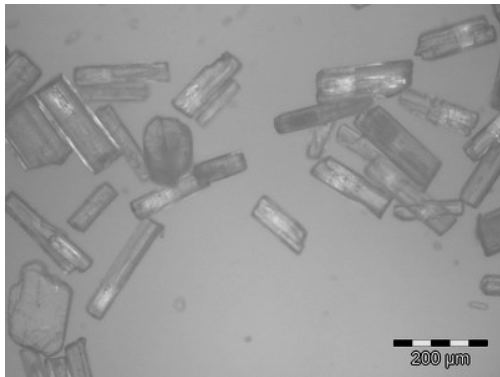


Picture 23 Technical gypsum3 after 4h in water picture taken by optical microscopy

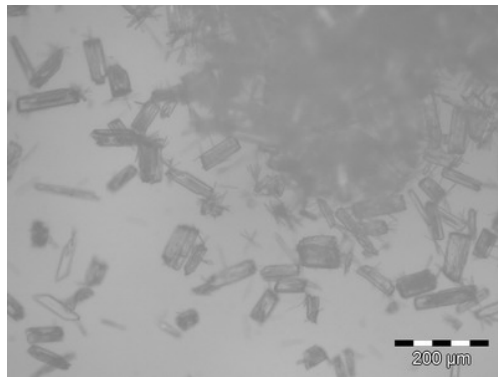
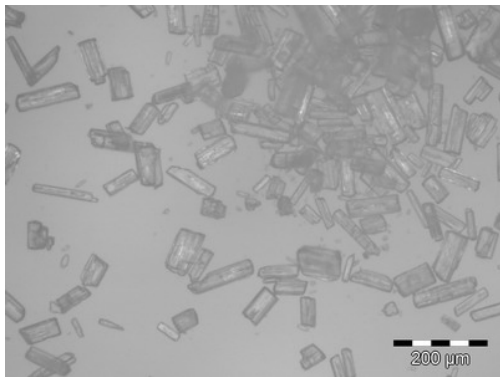


Picture 24 Technical gypsum3 after 4h in water picture taken by SEM

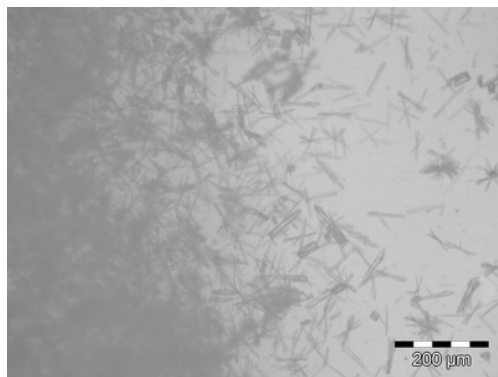
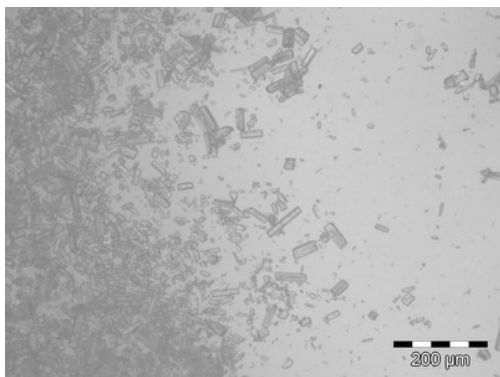
The influence of the sub-hydrate crystal dimension to the morphology of the gypsum crystals were also investigated, the results can be seen in pictures 25-30.



Pictures 25 and 26 α -sub-hydrate crystals $> 125\mu\text{m}$ one minute and 180 minutes after adding water



Pictures 27 and 28 α -sub-hydrate crystals $< 90\mu\text{m}$ $> 45 \mu\text{m}$ one minute and 120 minutes after adding water



Pictures 29 and 30 α -sub-hydrate crystals $< 45\mu\text{m}$ one minute and 120 minutes after adding water

Conclusions

It has been demonstrated that the hydration of gypsum has to be investigated by different methods in order to get a complete picture of the involved reactions. Every method influences the reaction in its own way and hence every method has its advantages and disadvantages. The optical microscopy works with a too high water/gypsum-ratio. The effect of this was measured by the heat flow calorimetry, and there was no influence on the reaction time detected. Optical microscopy could show the crystals by reacting and give an impression of the crystal behaviour. By SEM only the dried crystals could be detected. The advantage is the higher resolution in comparison to optical microscopy and by EDX the compounds of the crystals can be measured. By the *in situ* XRD there is much energy-input to the sample, but the reaction time is the same as measured by the other methods. With these methods the amount of the reacting substances can be measured very well. The sonic wave measurement can not be started when the reaction starts, because the sample has to be prepared outside the measurement cell. So the measurement starts with a delay of about 1 minute. This method is the best to analyse the setting time of plaster.

We could show that the morphology of the gypsum crystals vary from one technical gypsum to an other, and the differences between different charges of the same gypsum are most times very small. The detected crystal morphology is between long gypsum needles, large flat dove-tailed crystals and smaller crystals without a macroscopic structure.

The reaction of calcium sulphate sub-hydrates with water consists of three parallel steps. The dissolving of the sub-hydrate crystals, the growing of gypsum crystals and an inner hydration of sub-hydrates could be investigated.

The dimension of the sub-hydrate crystals has an influence to the gypsum after the reaction. Larger sub-hydrate crystals serve as substrate for the growing gypsum crystals, and the smaller sub-hydrate crystals accelerate the reaction and build longer needle-like gypsum crystals and do not work as much as growing substrate for the gypsum. An inner hydration was only investigated by crystals larger than about 60 μm .

Prospect

To join the advantages of optical microscopy and scanning electron microscopy the measurements would be done by environmental scanning electron microscopy.

To show the effect of additive to the crystal behaviour the optical microscopy, the sonic wave measurement, the *in situ* XRD-measurement and the heat flow calorimetry have to be tested with different additives like tartaric acid or citric acid.

To see the influence of the drying temperature in production of the β -sub-hydrate a gypsum should be dried in different temperature programs and measured by the mentioned methods. The drying could be done in the differential scanning calorimeter because with this tool an exact temperature program could be ensured and the sample mass would be enough for most of the methods.

The optical microscopy measurements have to be supplemented by measurements with a heating cell for the microscope. With this cell also the drying of gypsum could be investigated.

Literature

- [1] M.H. Le Chatelier : Crystalloids against colloids in the theory of cements, Trans. Faraday Soc. 14 (1919) 8.
- [2] I.A. Perederij: Theorie der Bildung, Erhärtung und Festigkeit von normalem Gips und hochfestem Gips GP, Chem. Techn. 8 (1956) 659.
- [3] E. Eipeltauer: Erzeugung von kriechfesten Hartgipsen, Zem.-Kalk-Gips 6 (1960) 259.
- [4] S.Cahtterji, W. Jeffrey: Crystal growth during hydration of $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, Nature 200, 463-464 (1993)
- [5] V.F. Komarov, A.V. Severin and I.V. Melikhov,"Fluctuations: Growth rate of gypsum crystals, Crystallography reports Volume 45 (2) 329-335 (2000)
- [6] Y. Sakalli, C. Pritzel, R. Trettin, Akustische Untersuchung des Einflusses der Kristallmorphologie auf die Festigkeitsentwicklung von Gipsen, Tagungsband der GDCh-Bauchemie-Tagung 343-352
- [7] C. Pritzel, R. Trettin, In situ Untersuchungen zum Reaktionsverlauf von Calciumsulfatsubhydraten mit Wasser, Tagungsband der GDCh-Bauchemie-Tagung 252-257