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Discrimination of bassanite and anhydrite III dehydrated from gypsum at different temperatures

S. Seufert*, C. Hesse, F. Goetz-Neunhoeffer, J. Neubauer

Geozentrum Nordbayern, Mineralogy, University of Erlangen-Nuernberg, Schlossgarten 5a, 91054 Erlangen, Germany
* sese@geol.uni-erlangen.de

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Abstract. Technical OPC normally contains mixed sulphate carriers in varying amounts. Gypsum (calcium sulphate dihydrate, $CaSO_4 \cdot 2\,H_2O$) is added to the clinker before the milling process and dehydrates partially to bassanite (calcium sulphate hemihydrate, $CaSO_4 \cdot 0.5\,H_2O$) and anhydrite ($CaSO_4$). The dehydration temperature and humidity affects the resulting calcium sulphates. Anhydrite exists in different polymorphs (anhydrite I-III) of which anhydrite III shows the highest reactivity in contact with H_2O. Due to different kinetics of the calcium sulphate phases, which strongly influence hydration, it is very important to be able to characterize the sulphate carrier composition in the cement and in applications with high sulphate content. This study could prove that it is possible to quantify bassanite and anhydrite III in samples of dehydrated gypsum by Rietveld refinement of XRD data especially in mixtures consisting of more than one calcium sulphate modification.

Introduction

Bassanite as well as anhydrite III are metastable phases in the system $CaSO_4$-H_2O [1]. Figure 1 shows the similarity of the crystal structures of bassanite and anhydrite III described by Bezou. Both structures consist of a crystal frame of Ca^{2+} ions and SO_4^{2-}tetrahedral with channels of 0.2 nm diameters. Those channels are partially filled with water in case of bassanite and empty in case of anhydrite III [2]. Bassanite is formed from gypsum at temperatures from 45 °C to 200 °C due to the loss of 1.5 mole H_2O per formula unit. Under ambient conditions exclusively the β-modifications of bassanite will be formed. Different polymorphic modifications of bassanite (α, β, β’) depending on synthesis conditions were reported [3].

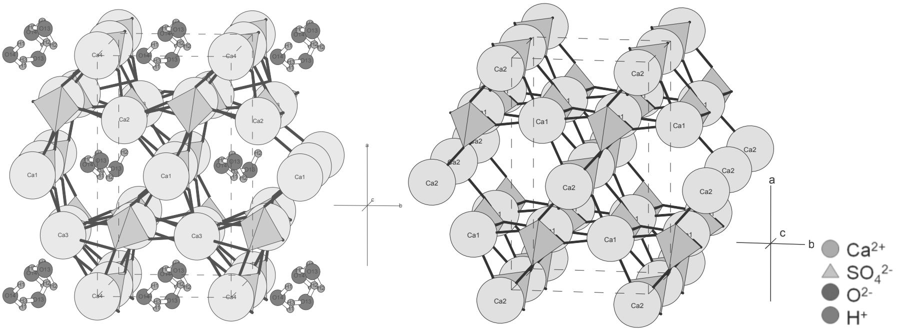

Figure 1. Bassanite (left) and anhydrite III (right) structure [2].

Heating at ambient conditions above temperatures of 100 °C leads to a loss of the remaining 0.5 mole H_2O per formula unit and therefore to the formation of H_2O-free β-anhydrite III [4]. In the present investigations thermogravimetric methods and XRD techniques using the Rietveld method were combined to carry out an accurate discrimination between the β-modifications of bassanite and anhydrite III that may be used in dry mortars. Objective was the setup of an analytical method for use in quality control during production of cements and sulphates.

Materials and methods

The dehydration of high purity gypsum (calcium sulphate dihydrate, Fluka, 99.9% purity) was performed in chamber furnaces at 85 °C up to 550 °C in air. The initial high purity gypsum was weighed in corundum crucibles of 60 ml size and dehydrated for 16 to 120 hours (dehydration time was dependant on dehydration temperature see table 1).

Table 1. Sample names, dehydration time and dehydration temperature.

Sample Name	Time of dehydration	Temperature of dehydration
Gypsum_85	120 h	85(±5) °C
Gypsum_120	120 h	120(±5) °C
Gypsum_180	16 h	180(±5) °C
Gypsum_250	16 h	250(±5) °C
Gypsum_380	16 h	380(±5) °C
Gypsum_550	16 h	550(±5) °C

For the dehydrated gypsum samples the loss on ignition was determined. To determine the experimental loss on ignition a reference gypsum sample was dehydrated at 800 °C and weighed out. The resulting value for the experimental loss on ignition value was 20.7 wt%. With this value all samples dehydrated at lower temperatures were corrected. Assuming that at temperatures of 85 °C and above the H_2O is chemically bound to calcium sulphate hemihydrate (with exactly 0.5 mole water), the amount of bassanite in the dehydrated samples could be recalculated by using equation (1).

$$m_{Bassanite} = m_{H_2O} + m_{H_2O} \cdot \frac{M(CaSO_4)}{0.5M(H_2O)} \tag{1}$$

m_{H_2O} = Mass of tared chemically bound H_2O in bassanite

$m_{H_2O} \cdot \frac{M(CaSO_4)}{0.5M(H_2O)}$ = Mass of chemically bound calcium sulphate in Bassanite

$M(CaSO_4)$ = 136.1576 g/mole; $0.5M(H_2O)$ = 9.00767 g/mole

To avoid any reaction of the dehydrated gypsum samples with air humidity, the powders were instantly transferred to small press-on lid pots, sealed with parafilm and stored in an exiccator above silica gel. Preparation of the dehydrated gypsum samples for X-ray investigations was carried out at 7 % relative humidity in a glove box. The sample was prepared in a D5000 sample holder and covered by Kapton brand X-ray film to prevent further transformation reactions (figure 2). The preparation was performed in the glove box to minimize reactions due to ambient humidity.

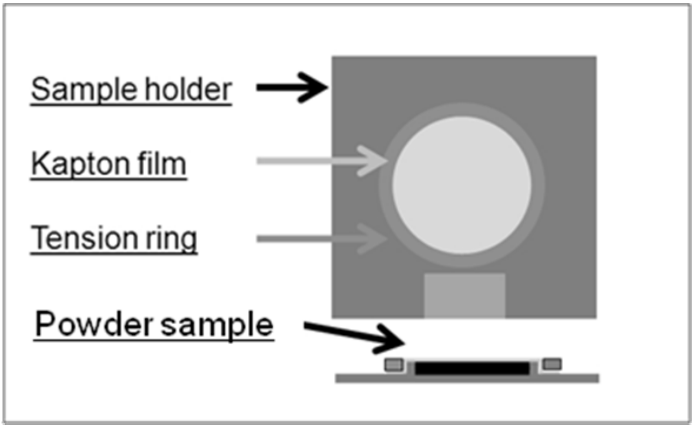

Figure 2. Scheme of D5000 sample holder covered with Kapton film.

Phase composition of the samples was examined at room temperature by quantitative X-ray powder diffraction (XRPD) with a Siemens D5000 diffractometer with CuKα X-ray radiation, secondary monochromator and a scintillation detector. The scanning range was 10° - 60° and the scanning time was 9 seconds in total. All samples were measured at an ambient temperature of 22 °C (± 2 °C). Rietveld refinement was performed using the structural models (ICSD) of all occurring calcium sulphate phases and the TOPAS software (V 3.0 Bruker AXS). Additionally the structures data for bassanite and anyhdrite III from Christensen et al. [7] were applied. Table 2 shows the used structure data for Rietveld refinement.

Table 2. Structures used for Rietveld refinement.

Phase	ICDD-PDF-No.	ICSD-No.	Author [ref.]
gypsum	33-0311	92567	Schofield [5]
bassanite	41-0224	79529	Bezou et al. [2], Christensen et al. [7]
anhydrite III	41-0224	79527	Bezou et al. [2], Christensen et al. [7]
anhydrite II	37-1496	16382	Kirfel [6]

Refined parameters were: scale factor, zero displacement, background as Chebychev polynomial of 5th grade, crystallite size and lattice parameters for anhydrite III and anhydrite II. Lattice parameters of bassanite were kept fix in order to achieve stable refinement results. Especially in samples with a low bassanite content (calculated from loss on ignition) fixing of the lattice parameters of bassanite is crucial. Since Kapton film was used to cover the samples during measurement it was necessary to correct the background with a manually generated peak phase for the Kapton film.

Results

All investigated powders consisted of at least two different calcium sulphates. Small amounts of less reactive anhydrite II were found in all dehydrated gypsum samples even at lower temperatures. With the chosen refinement method it was possible to discriminate highly reactive anhydrite III from bassanite in diffraction patterns measured under application-oriented conditions at room temperature. Figure 3 and 4 show the refined data set of gypsum dehydrated at 180 °C with high anhydrite III content refined with different structures for bassanite and anhydrite III from two different authors [2,7]. The differences in Rietveld results by exchanging the structures of bassanite and anhydrite III respectively were smaller than the assumed error. In figure 3 and 4 the discrimination of the two phases is visible due to slightly different peak positions of bassanite and anhydrite III.

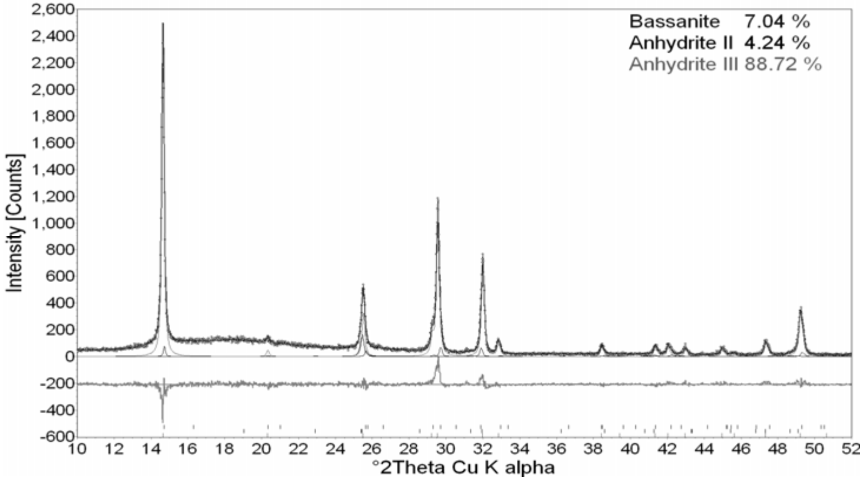

Figure 3. Rietveld refinement of dehydrated gypsum at 180 °C with refined structures of Bassanite[7], Anyhdrite III [7] and Anhydrite II [6]. $R_{Bragg\text{-}Bassanite}=7.7\%$, $R_{Bragg\text{-}Anhydrite\ II}=2.1\%$, $R_{Bragg\text{-}Anhydrite\ III}=7.6\%$, $R_{wp}=14.4\%$.

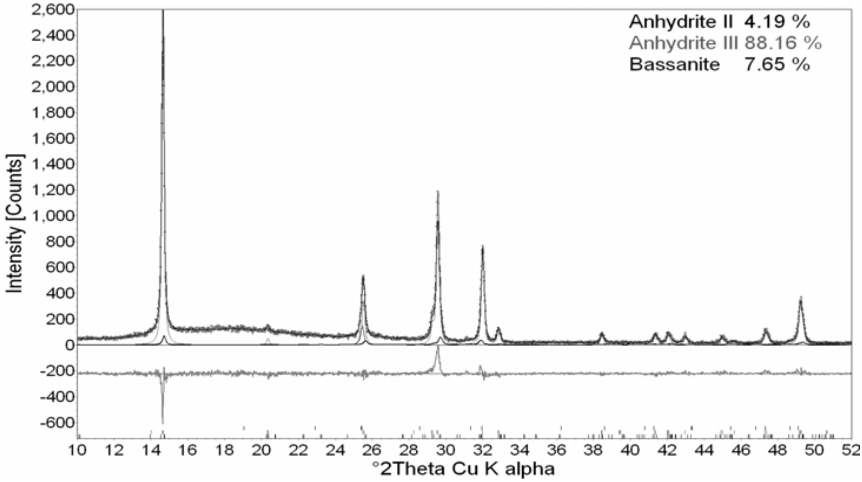

Figure 4. Rietveld refinement of dehydrated gypsum at 180 °C with refined structures of Bassanite[2], Anyhdrite III [2] and Anhydrite II [6]. $R_{Bragg\text{-}Bassanite}=6.8\%$, $R_{Bragg\text{-}Anhydrite\ II}=2.9\%$, $R_{Bragg\text{-}Anhydrite\ III}=7.9\%$, $R_{wp}=14.6\%$.

The determined loss on ignition of the dehydrated gypsum samples showed increasing anhydrite III content at the expense of bassanite with increasing temperature. Anhydrite III is formed at temperatures of 120 °C, and transformed to anhydrite II at higher temperatures (>180 °C). Table 3 shows the results of Rietveld refinement. In case of bassanite the calculated content from loss on ignition (LOI) are comparable to the results from the Rietveld refinement. Only for the sample of gypsum dehydrated at 120 °C it can be assumed that an early rehydration process of anhydrite III to bassanite is responsible for the different results of Rietveld refinement compared to the calculated bassanite content from loss of ignition.

Table 3. Results of Rietveld refinement compared to calculated bassanite content from LOI.

Dehydration Temperature	bassanite [wt%]		anhydrite III [wt%]	anhydrite II [wt %]
	(calculated from LOI)	6 % rel. humidity	6 % rel. humidity	6 % rel. Humidity
85 °C	95.7	95.2	0.6	4.2
120 °C	11.0	20.9	75.8	3.3
180 °C	6.0	7.6	88.2	4.2
250 °C	3.8	3.2	73.2	23.6
380 °C	2.1	2.3	16.7	81.0
550 °C	0.0	0.0	0.0	100.0

Conclusion

A discrimination of bassanite and anhydrite III in the same powder via Rietveld refinement can be accomplished in application-oriented XRD patterns. Moreover, the investigations showed the hygroscopic character of dehydrated calcium sulphates and the need of storage under exclusion of humidity, especially in case of anhydrite III. High humidity causes an instant transformation of anhydrite III to bassanite. Rietveld refinement could be utilized to differentiate calcium sulphates with very similar crystalline structure and to measure in-situ transformation processes by rehydration in pure calcium sulphates. Discrimination of anhydrite III and bassanite was performed in powders of high purity. The determination of anhydrite III besides bassanite in dry mortar mixtures containing 20 Ma% and more sulphate is possible by Rietveld refinement. In cement applications with lower sulphate content the discrimination via Rietveld refinement could be more difficult. Furthermore, other investigations showed that a rehydration of anhydrite III to bassanite even through the Kapton film of the sample holder can not be avoided.

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