Cement and Concrete Research 39 (2009) 936–941

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Quantitative determination of anhydrite III from dehydrated gypsum by XRD

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

Mineralogy Geozentrum Erlangen, University of Erlangen-Nuernberg, Schlossgarten 5 a, 91054 Erlangen, Germany

ARTICLE INFO

Article history:
Received 29 July 2008
Accepted 18 June 2009

Keywords:
Portland cement
Hydration
X-ray diffraction characterization
Calcium sulfate

ABSTRACT

Technical OPC contains mixed sulfate carriers in varying amounts. Gypsum and anhydrite are added to the clinker during the milling process where the gypsum dehydrates partially to bassanite and anhydrite. Due to different hydration kinetics of these phases, it is crucial to be able to characterize the composition of sulfate in a cement system to reach an optimal and reproducible cement hydration. In the current paper different calcium sulfate compositions are investigated by XRD methods in order to identify phase content. Special focus is put on the discrimination of the hemihydrate (bassanite) and anhydrite III as well as on transformation processes of anhydrite III through ambient humidity.

1. Introduction

Dehydrated calcium sulfates play a major role in the Portland cement hydration processes especially at early ages. Besides the amount of sulfate in a cement system its solubility and availability is a crucial factor influencing the formation of the first hydration products like ettringite and monophases in the slurry. Solubility relations in the system $CaSO_4$–H_2O have been investigated by different authors [1–3]. Gypsum (calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$) is the most aqueous phase in the system $CaSO_4$–H_2O and, besides anhydrite II, the stable phase under ambient atmospheric conditions. With increasing temperature gypsum starts to dehydrate and form calcium sulfates with lower H_2O content. The dehydration process proceeds stepwise and leads to metastable calcium sulfate phases. Bassanite (calcium sulfate hemihydrate, $CaSO_4 \cdot 0.5\ H_2O$) is formed at the loss of 1.5 mol H_2O per formula unit with respect to gypsum. Hemihydrate exists in different morphologic forms (α, β and β′). Studies by thermo gravimetric methods showed a dependence concerning water pressure and the resulting surface area of the synthesized hemihydrates [4–6,10]. The β-modification of hemihydrate is formed under ambient conditions at temperatures ranging from 45 °C to 200 °C [7]. In contrast to the α-modification the β-modification is microcrystalline with a high specific surface area [16]. Further heating of bassanite above temperatures of 100 °C leads to soluble anhydrite (anhydrite III, $CaSO_4$) [9]. Anhydrite III exists analog with bassanite in three different modifications (α, β and β′). Continued heating above 200 °C leads to less soluble anhydrite (anhydrite II) [8]. A fifth phase—anhydrite I—is known to be formed from anhydrite II at temperatures above 1180 °C [9]. Former investigations [10] showed the relation between temperature and phase formation during heating processes. A differentiation of bassanite and anhydrite III was not accomplished. The structures of bassanite and anhydrite III are considered to be very similar as both structures provide structural channels of 0.4 nm diameter. In the case of bassanite those channels are partially filled with H_2O molecules and they are empty in case of anhydrite III [4].

Table 1
Sample names, dehydration temperatures, dehydration times of the investigated calcium sulfate powders.

Sample name	Time of dehydration	Temperature of dehydration
G_85	120 h	85(±5) °C
G_120	120 h	120(±5) °C
G_180	16 h	180(±5) °C
G_250	16 h	250(±5) °C
G_380	16 h	380(±5) °C
G_550	16 h	550(±5) °C

Table 2
Measurement conditions for single range and multi range measurements of dehydrated gypsum samples.

	Single range	Multi range
Type of diffractometer	Siemens D5000 with secondary monochromator	
Type of X-ray radiation	Cu Kα	
Voltage/Current	40 kV/30 mA	
Type of detector	Scintillation detector	
Primary divergence slit	0.5°, fix	
Sec. divergence slit	0.5°, fix	
Ambient temperature	22 °C (±2 °C)	
Scanning range(2θ)	10°–60°	10°–45°
Step size (2θ)	0.02°	
Time per step	3 s	1 s

* Corresponding author.

0008-8846/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2009.06.018

Table 3
ICDD-PDF and ICSD data used for quantitative and qualitative analysis of the diffraction patterns.

Phase	ICDD-PDF-No.	ICSD-No.	Author [Ref.]
Gypsum	33-0311	92567	Schofield [14]
Bassanite	41-0224	79529	Bezou [4]
Anhydrite III	41-0224	79527	Bezou [4]
Anhydrite II	37-1496	16382	Kirfel [15]

Consequently the refinement from XRD data is not trivial. The dehydration of gypsum is a reversible process. When water is added, the empty channels in the anhydrite III structure are refilled with H_2O molecules forming bassanite without dissolution [12]. Gypsum is formed from a saturated calcium sulfate solution [13]. Due to the different crystal structure of anhydrite III the anhydrite II will not be rehydrated by forming bassanite in solutions, but directly dissolve and precipitate as gypsum instead. The different rehydration behavior of the considered calcium sulfates consequently leads to differences in heat flow development [11]. In the present paper the influence of temperature increase on gypsum powder and the characterization of the received phases are reported. Since all dehydration processes were realized under atmospheric pressure, only β-modifications of bassanite and anhydrite III were investigated which is close to technical conditions during cement milling. Calorimetric and XRD techniques were combined, whereas special emphasize was put on the differences of β-bassanite and β-anhydrite III in XRD data.

2. Materials and methods

2.1. Synthesis of different calcium sulfates by dehydration

Gypsum (calcium sulfate dihydrate, Fluka, 99.9% purity) samples were dehydrated at temperatures from 85 up to 800 °C 25 g of substance was weighed in corundum crucibles of 60 ml size and dehydrated in two different furnace types to cover the complete

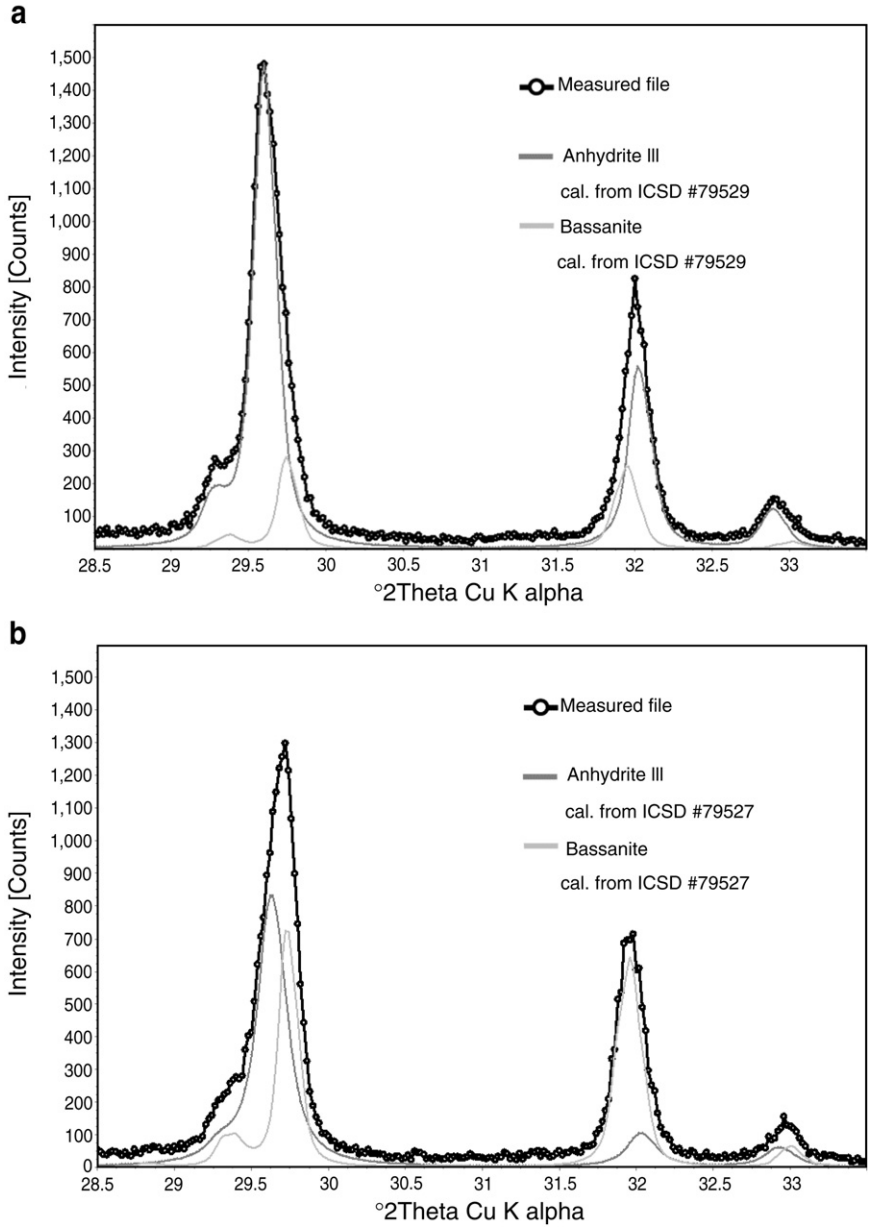

Fig. 1. XRD-pattern of dehydrated gypsum with a) high anhydrite III content and b) high bassanite content. Calculated ICSD patterns of bassanite and anhydrite III [4] from Rietveld refinement.

temperature range. The furnaces were calibrated with thermo elements. After the dehydration process the samples were cooled down to ambient temperature under exclusion of humidity and the weight loss was determined. The powders were transferred to press-on lid pots. Instant sealing with parafilm and storing in a desiccator above silica gel could avoid reaction of the samples with air humidity. Table 1 shows the sample names dehydration temperatures and furnace identification.

Dehydrated gypsum at 800 °C was investigated to determine the total loss on ignition of gypsum. Theoretically the loss of chemically bound H_2O should make a difference of 20.93 wt.%. The experimental loss on ignition (LOI) was determined to be 20.7 wt.%. The calcium sulfates dehydrated at the different temperatures were corrected with respect to the experimental value and the remaining H_2O content in the samples was determined. Assuming that at temperatures of 85 °C and higher the H_2O is chemically bound to calcium sulfate hemihydrate

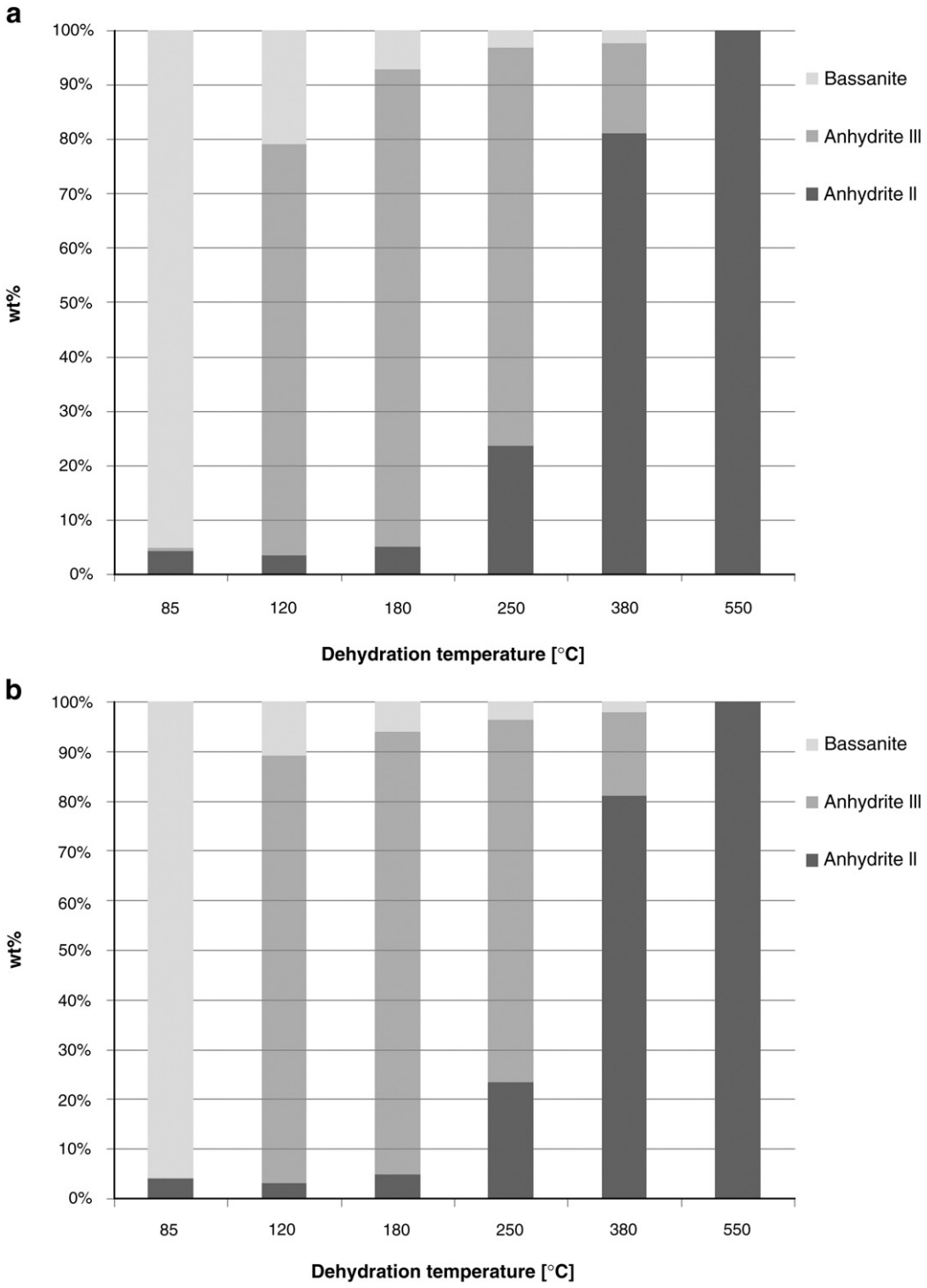

Fig. 2. Phase content of dehydrated gypsum in dependence of temperature calculated from Rietveld refinement, a) preparation in a glove box with 6% relative humidity, b) Bassanite content calculated from loss on ignition.

(with exactly 0.5 mol water), the amount of bassanite in the dehydrated samples could be recalculated by using Eq. (1).

$$wt_{\text{Bassanite}} = wt_{H_2O} + wt_{H_2O} \cdot \frac{M(CaSO_4)}{0.5\text{M}(H_2O)}$$

wt_{H_2O} = Weight of tared water chemically bound in bassanite

$$wt_{H_2O} \cdot \frac{M(CaSO_4)}{0.5\text{M}(H_2O)} = \text{Weight of calcium sulfate chemically bound in bassanite} \quad (1)$$

For calculation issues the remaining H_2O content after the burning process was considered to be fully bound to bassanite. All synthesized calcium sulfates were furthermore investigated by XRD methods.

2.2. Phase analysis of the dehydrated calcium sulfates

The dehydrated calcium sulfate samples and the original gypsum were investigated by X-ray powder diffraction (XRD) and analyzed with respect to phase content and purity. Gypsum was prepared under ambient room conditions in a sample holder. The other samples were transferred to a sample holder under ambient humidity (relative humidity of 47% ± 3%) in a first run and covered with 7 μm Kapton® polyimide film. Three data sets of each sample were measured by XRD. The measurement time was 125 min. In a second run the samples were transferred to the sample holder in a glove box with a relative humidity of 6% ± 3% (dried with silica gel) and covered with Kapton polyimide film in the glove box. The measurements were reproduced twice, whereas the first measurement of every sample was a continuous long time measurement over more than 14 h, to detect stability of the sample. The measurement conditions are listed in Table 2.

All XRD measurements were reproduced twice. The evaluation of the data sets was carried out with the software EVA (Diffrac Plus, Version 12.0, Bruker Analytical X-Ray Systems) for qualitative analysis and TOPAS (V 3.0 Bruker AXS) for quantitative analysis with Rietveld method. Table 3 shows the used phases with ICSD numbers and PDF numbers, respectively whereas in case of anhydrite III and bassanite the same ICDD-PDF structure was used.

For the single Rietveld refinement a background Chebychev of 5th order was chosen and the zero error was refined. The scale factor and crystallite size parameter were also refined. Microstrain was fixed at 0.1 and the lattice parameters for anhydrite III and anhydrite II were refined. In cases with either low bassanite or low anhydrite III content it was necessary to fix the lattice parameters, crystallite size, and microstrain of bassanite in order to achieve stable refinement result. For analysis of the long time XRD measurements the first file was refined as described above and the obtained lattice parameters of anhydrite II and anhydrite III were kept fixed and used for refinement of the other long time ranges. Since Kapton polyimide film was used to cover the samples during measurement it was necessary to correct the background with a peak phase generated for the polyimide film.

3. Results and discussion

3.1. Quantitative phase analysis

The investigation of the original untreated gypsum via XRD and Rietveld method proved that no detectable amounts of bassanite or anhydrite were present. In the dehydrated samples it was assumed that no subhydrate $(CaSO_4\ (H_2O)_x$ with $x>0.5)$ was stabilized due to synthesis conditions. Both of the structural similar phases, anhydrite III and bassanite, could be refined in the XRD patterns. Fig. 1a shows the calculated XRD-pattern of anhydrite III and bassanite in the 2 Theta range of 28.5 °2θ–33.5 °2θ [4] of the Rietveld refinement of a dehydrated gypsum. The anhydrite III structure as well as the bassanite structure is fitted to the measured data set. In the sample shown in Fig. 1a the anhydrite III content was higher than the bassanite content. Fig. 1b shows a sample with higher bassanite content than anhydrite III content and the corresponding fitting of the structures after Rietveld refinement.

In Fig. 2a the phase composition of samples G_85 to G_550 prepared under 7% relative humidity in a glove box and evaluated with the Rietveld method are compared. Since the uncertainty of the Rietveld investigations was 2 wt.% an illustration in the figures was not resolved. For all temperatures a mixture of two or three calcium sulfates was found. Bassanite content decreases rapidly from 95 wt.% to 2 wt.% with raising temperature from 85 °C to 380 °C. Since hemihydrates are not formed at temperatures above 200 °C [8] the measured hemihydrate must be a result of phase transformation during sample cooling or sample handling. Metastable anhydrite III is known to have a strong hygroscopic character [16] and is rapidly transformed into bassanite under not completely dry conditions. Even the short preparation time (5 min) led to detectable bassanite contents in samples from dehydration over 200 °C.

Compared to the calculated bassanite content from residual water as shown in Fig. 2b, preparation at 6% relative humidity in the glove box led to similar reliable bassanite values. It can be postulated that dehydration of gypsum at a temperature of 85 °C for 120 h almost exclusively leads to bassanite (96 wt.% bassanite, 4 wt.% anhydrite II). The reverse reaction must be kinetically hindered as no gypsum was detected by Rietveld investigation. The main effect of temperature in the interval from 85 °C to 180 °C is further dehydration of bassanite to anhydrite III with a similar structure. At higher temperatures above 180 °C the effect is to transform anhydrite III into stable but less reactive anhydrite II. Even at temperatures higher than 120 °C the occurrence of bassanite in XRD files must be due to transformation processes after the dehydration while cooling and storing.

The Rietveld refinement of sample G_85 to G_550 prepared at a relative humidity of 47% pointed out the hygroscopic character of anhydrite III. The transformation process of anhydrite III to bassanite was strongly accelerated as in the samples prepared under 47% relative humidity, 20 wt.% more bassanite on average were detected than in the samples prepared at 6% relative humidity. Table 4 summarizes the results of Rietveld refinement at 47% relative humidity and 6% relative humidity.

Table 4
Rietveld refinement data.

Dehydration temperature	Bassanite [wt.%]			Anhydrite III [wt.%]		Anhydrite II [wt.%]	
	(calculated from LOI)	47% rel. humidity	6% rel. humidity	47% rel. humidity	6% rel. humidity	47% rel. humidity	6% rel. humidity
85 °C	95.7	95.5	95.2	0.0	0.6	4.5	4.2
120 °C	11.0	39.6	20.9	57.7	75.8	2.7	3.3
180 °C	6.0	31.6	7.2	62.4	87.8	6.0	5.0
250 °C	3.8	15.9	3.2	60.0	73.2	24.1	23.6
380 °C	2.1	5.8	2.3	10.1	16.7	84.1	81.0
550 °C	0.0	0.0	0.0	0.0	0.0	100.0	100.0

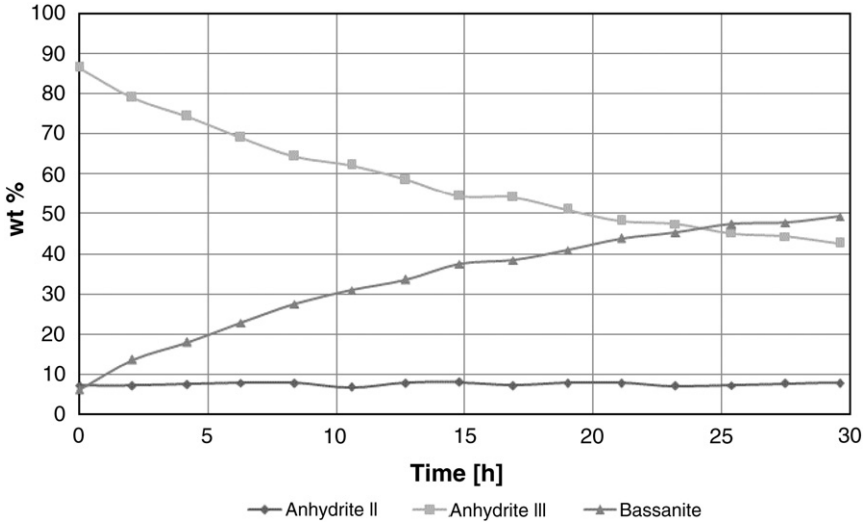

Fig. 3. Transformation of anhydrite III to bassanite within 30 h, gypsum dehydrated at 180 °C, (sample G_180), the sample holder is covered with 7 μm thick Kapton polyimide film, measurement at 23 °C.

3.2. Rehydration of dehydrated gypsum in dependence of time (0–30 h)

Special preparation conditions in a glove box with a relative humidity of 6% were chosen to make sure that the samples dehydrated from gypsum powder were prevented from rehydration. With this preparation method an XRD recording of the original and not of the rehydrated samples could be ensured. In Fig. 3 the phase content over time is plotted for gypsum dehydrated at 180 °C (sample G_180). The size of the mark in the diagram represents the maximum error of 2 wt. % content. Attention should be paid to the fact, that each data file and the refined phase content represents an average determination during the 2 h of XRD data recording.

As shown in Fig. 3 the anhydrite III content in the sample of gypsum dehydrated at 180 °C, decreases from 86 wt.% at start of the measurements to 43 wt.% after 29.5 h. Within the same time the amount of bassanite increases from 6 wt.% to 49 wt.%. A complete barrier against diffusion of the H_2O into the sample by covering it with the 7 μm thick Kapton polyimide film was not possible. Compared to the same sample (G_180) prepared at 47% relative humidity, the sample prepared under 6 % relative humidity in the glove box reaches the similar bassanite content (31 wt.%) after 11 h. The incorporation of water and therefore transformation of anhydrite III to bassanite proceeds continuously, but the phase transformation rate decelerates with increasing investigation time. The effect can be explained by claiming that H_2O molecules are incorporated into the sample grains—especially at the top after diffusing through the Kapton polyimide film. When the anhydrite III areas close to the Kapton polyimide film are transformed to bassanite, the transformation of the underlying powder is more and more decelerated. As expected the phase content of stable anhydrite II does not change significantly during the measured time. Measurements reproduced for samples with similar initial quantities of anhydrite III at 120 °C and 250 °C showed comparable results. At higher burning temperatures the anhydrite III content was very low, therefore long time measurements for these samples were not performed. An apparent peak shift is detectable in the in-situ levelplot. Fig. 4 shows this shift in balance point of anhydrite III synthesized at 180 °C (Sample G_180) over time. The dotted lines represent the actual anhydrite III peak position. This development was also observed inverse in former investigations during heating processes [17].

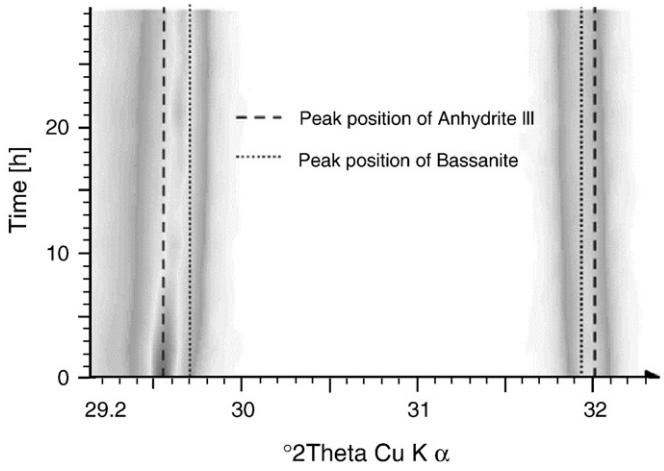

Fig. 4. In-situ levelplot of anhydrite III to bassanite transformation with indicated peak positions of the pure anhydrite III and bassanite phases, gypsum dehydrated at 120 °C, (sample G_120), sample holder covered with Kapton polyimide film, 23 °C.

4. Conclusion

Dealing with XRD data of high quality and high resolution, it is possible to differentiate bassanite and isostructural anhydrite III. Samples with low contents of anhydrite III and bassanite respectively require a fixing of the lattice parameters of bassanite to stabilize the results of quantification. The dehydration temperature of gypsum strongly influences phase composition of the resulting calcium sulfates and, in consequence reactivity of the samples. All samples consisted of at least two calcium sulfate phases with different reactivity. It was not possible to synthesize single phase samples or prevent them from transformation during XRD investigation within 24 h. In case of anhydrite III a transformation into bassanite can only be avoided by great efforts in sample handling and dry storing conditions. The transformation process in pure calcium sulfate samples can be well examined by XRD methods. The results of the experimental work presented above shows the importance of constant storage conditions in cement applications.

References

[1] M. Murat, M. Foucault, Sulfates de Calcium et Materiaux Derivés, Colloq. Intern. de la RILEM, Saint Rémy les Chevreuse, France, 1977 546–548.
[2] K.U.G. Raju, G. Atkinson, The thermodynamics of “scale” mineral solubilities. 3. Calcium sulfate in aqueous NaCl, J Chem Eng Data 35 (1990) 361–367.

[3] N. Møller, The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na–Ca–Cl–SO4–H2O system, to high temperature and concentration, Geochim Cosmochim Acta 52 (1988) 821–837.
[4] C. Bezou, A. Nonat, J.-C. Mutin, A. Nørlund Christensen, M.S. Lehmann, Investigation of the crystal structure of γ-$CaSO_4$, $CaSO_4 \bullet 0.5\ H_2O$, and $CaSO_4 \bullet 0.6\ H_2O$ by powder diffraction methods, Journal of Solid State Chemistry 117 (1995) 165–167.
[5] M. Frick, H.J. Kuzel, Röntgenographische und thermoanalytische Untersuchungen an Calciumsulfat-Halbhydrat, Fortschr. Mineral 60 (1982) 79–80.
[6] J.J. Gardet, B. Guilhot, M. Soustelle, Hydrated forms of calcium sulfate, Bull Soc Chim Fr 10 (1970) 3377–3382.
[7] D.A. Powell, Transformation of the α- and β-forms of calcium sulfate hemihydrate to insoluble anhydrite, Nature 182 (1958) 792.
[8] Gipsdatenbuch, Bundesverband der Gipsindustrie e.V., 2003.
[9] J. Bensted, S. Prakash, Investigation of the calcium sulphate–water system by infrared spectroscopy, Nature 219 (1968) 60–61.
[10] W. Abriel, K. Reisdorf, Dehydration reactions of gypsum: a neutron and X-ray diffraction study, Journal of Solid State Chemistry 85 (1990) 23–30.
[11] H.-J. Kuzel, Heats of hydration of the α-calcium sulfates, N. Jb. Min., Abh 156 (1987) 155–174.
[12] J. D'Ans, D. Bredtschneider, H. Eick, H.-E. Freund, Calcium sulfate, Kali Steinsalz 9 (1955) 17–38.
[13] L. Amathieu, R. Boistelle, Crystallization kinetics of gypsum from dense suspension of hemihydrate in water, J Cryst Growth 88 (1988) 183–192.
[14] P.F. Schofield, C.C. Wilson, K.S. Knight, I.C. Stretton, Temperature related structural variation of the hydrous components in gypsum, Zeitschrift fuer Kristallographie 215 (2000) 707–710.
[15] A. Kirfel, G. Will, Charge density in anhydrite, $CaSO_4$, from X-ray and neutron diffration measurements, Acta Crystallographica B 36 (1980) 2881–2890.
[16] Ullmann's Encyclopedia of Industrial Chemistry, Vol A 4 (1985) 555–584.
[17] R.J. Cernik, P. Barnes, G. Bushnell-Wye, A.J. Dent, G.P. Diakun, J.V. Flaherty, G.N. Greaves, E.L. Heeley, W. Helsby, S.D.M. Jacques, J. Kay, T. Rayment, A. Ryan, C.C. Tang, N.J. Terrill, The new materials processing beamline at the SRS Daresbury, MPW6.2, J Synchrotron Radiat 11 (2) (2004) 163–170.