

Study of gypsum by PDSC

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Abstract Calcium sulfate dihydrate has been widely characterized by both differential scanning calorimetry and thermogravimetry (TG). Two dehydration processes were reported to be partially overlapping. High resolution TG and water vapor self generated atmosphere pin-hole lid strategies were used to increase the resolution of both dehydration processes. In this study, isobaric experiments were carried out in a pressure differential scanning calorimetry cell. The approach consisted in combining the pin-hole lid with different pressures with nitrogen atmosphere. Resolution was improved at moderately low pressures. At higher pressures other processes were observed.

Keywords Gypsum · PDSC · Pressure · Crystallization · Vapor · Water

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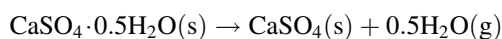
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Introduction

Gypsum is extensively used in industry, mostly as plaster of Paris. Polymer modifiers are frequently incorporated into the plaster to improve its toughness, gloss or to reduce the porosity. Gypsum is also mixed with cement to avoid immediate settling of the cement, although it also affects the strength and volume stability of the product [1]. Control of the reaction rate of tricalcium aluminate (C3A), the constituent of cement that reacts most rapidly with water, is most commonly achieved through the addition of gypsum (sometimes hemihydrate is also used) to commercial Portland cement [2]. The composition of gypsum is calcium sulfate, displaying approximately 3% equilibrium moisture and about 20 mass% of chemically bound and/or combined crystallization water. The chemical formula is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (calcium sulfate dihydrate) [3]. Thermal analysis techniques, such as combined differential scanning calorimetry (DSC)/thermogravimetry (TG), are very suitable to characterize dehydration processes of gypsum [4, 5] and other mineral compounds [6]. On heating, gypsum undergoes two partially overlapping endothermic processes, which may be observed by both TG and DSC [7]. At atmospheric pressure, these processes are centered at close temperatures and were described as two sequential dehydration steps. The mass of water evolved in each of these steps is described by [8, 9].



One-step process was observed to occur at negligible $\text{P}_{\text{H}_2\text{O}}$ in non-isothermal condition and below 100 °C in isothermal condition, while two-step process occurs at autogenous $\text{P}_{\text{H}_2\text{O}}$ in non-isothermal condition and above

100 °C in isothermal condition [5]. Thermal decomposition of gypsum is very dependent on the experimental conditions such as particle size of the sample, atmosphere, heating rate. Thus, slow heating rates as well as low water vapor partial pressures determine the formation of β -CaSO₄ III, a product with a high specific surface area. Its subsequent heating leads to the compact α -CaSO₄ IV. These two iso-structural phases were observed under specific conditions: water saturated ambient or vacuum [10, 11]. The α -phase is obtained by gypsum dehydration at more than 97 °C in water-saturated environment. On the other hand, β -phase is obtained by heating at 100 °C, in vacuum or under an unsaturated moisture environment [12]. Hydration of calcined gypsum is also of interest and a calorimetric method for the separation of different hydration reactions was recently proposed [13]. The influence of the pressure on the thermal behavior of gypsum was investigated by differential thermal analysis (DTA) in the range of pressures below 1 atm [14] and by Raman spectroscopy and angle-dispersive X-ray diffraction attached to an electrically heated diamond anvil cell (DAC) at high pressures [15]. The aim of this study is to investigate by pressure differential scanning calorimetry (PDSC) the dependence of the thermal behavior on pressure in the range from 1 to 70 bar.

Experimental

Gypsum samples were obtained from commercial plaster of Paris, which was mixed with water to re-form into gypsum. The material was manually reduced to powder in a porcelain mortar. Powder samples were used for thermal and X-ray diffraction analysis.

Simultaneous TG-DSC were performed in a Rheometric STA 1500 (STA) with a 50 mL/min flow of air. Open and pin-hole crucibles were used. The heating rate was 5 °C/min. PDSC experiments were performed in a TA Instruments MTDSC Q-2000 furnished with a pressure cell. The instrument was calibrated at 34 bar and tests with indium were made at several pressures to check the validity of the temperature and enthalpy measurements in the range from 1 to 70 bar. Sample experiments were performed with open and pin-hole aluminum crucibles at constant pressures of 1, 16, 34, 50, and 67 bar. Some additional pin-hole experiments were performed at 2, 8, and 10 bar. A nitrogen flow of 90 mL/min was kept along the experiments. Sample size was about 10 mg. The thermal programs consisted of linear heating ramps at 5 °C/min, from 40 to 380 °C. Two additional experiments were performed in the same conditions but stopped at specific temperatures of 157 and 180 °C. These experiments were followed by cooling ramps at 5 °C/min.

The original sample of gypsum and the samples that underwent thermal treatments were structurally investigated by X-ray diffraction. In order to obtain suitable quantities of sample for XRD analysis, special non sealed aluminum containers were prepared to apply thermal treatments into the PDSC cell. Samples of about 200 mg were packed into aluminum foil. No reference crucible was used. It is well known that resolution decreases when increasing sample size. Thus, a lower heating rate was used to improve resolution. Concretely, 1 °C/min heating rate was applied from room temperature to some specific temperatures. The pressure was 67 bar and the samples were let to cool at the same pressure.

Results and discussion

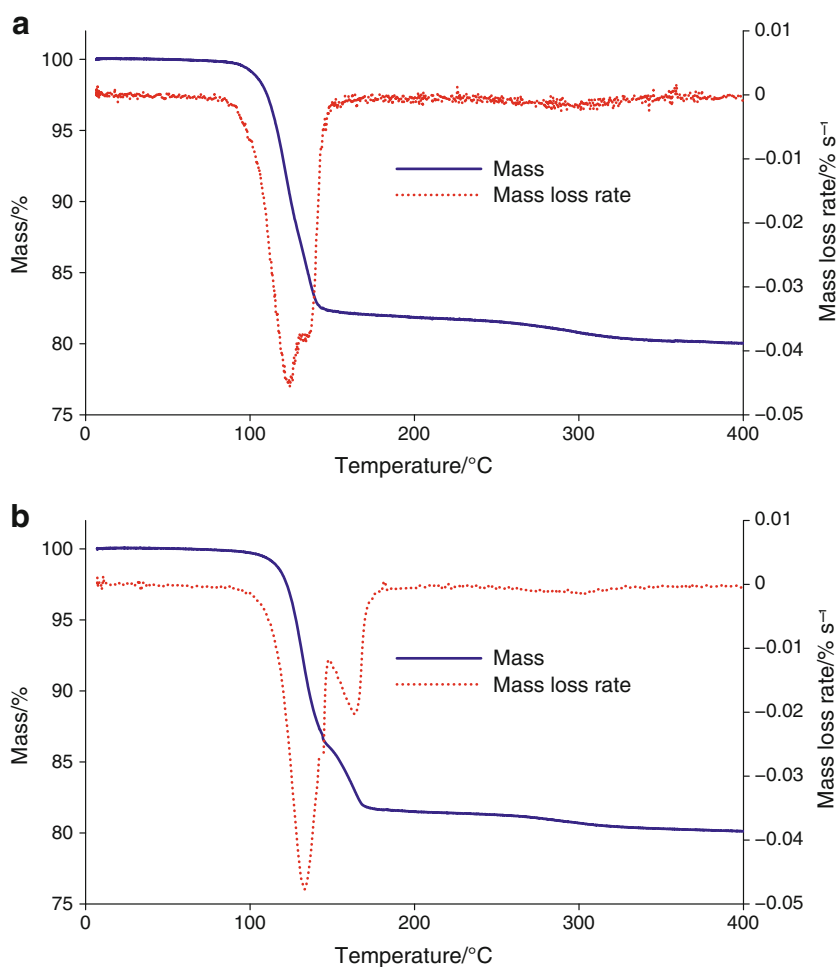
Figure 1 shows the TG and time derivative TG (DTG) plots obtained with open (a) and pin-hole (b) crucibles. The mass loss in the range from room temperature to 200 °C corresponds to full dehydration of gypsum and is practically the same in both cases. This process is shifted to higher temperatures in the pin-hole case. There is also a mass loss step in the 250–350 °C range. This mass loss accounts for a 1.5% and can be easily assigned to the polymer modifier. The residue at 400 °C is 80%.

Considering that plaster of Paris is typically composed of gypsum, silica and polymer modifier, the resulting composition would be: gypsum 87.5%, silica 11.0%, and polymer modifier 1.5%. Nevertheless, considering that, as will be explained below, the fresh sample also contains a small amount of anhydrite, the 11% inert fraction (which does not decompose in this range of temperature) would account for silica and that small amount of anhydrite.

Figure 2 shows an overlay of gypsum DSC curves obtained with open crucibles in STA at atmospheric pressure and in DSC at 1, 16, 34, 50, and 67 bar. It can be observed that a complete separation, with baseline recovery between both processes, was obtained at pressures over 34 bar. Table 1 shows the enthalpy and area percent values obtained at different pressures. For pressures lower than 34 bar, since both peaks overlap, estimations of the partial areas and enthalpies were obtained by the Fityk convolution software. It is important to notice that, in general, the percent rate of the partial areas is kept at different pressures, but the higher the pressure, the lower the enthalpy values, as shown in Table 1. The influence of the type of pans (hermetic, pin-hole, and standard) is extensively discussed in the literature [16].

Figure 3 shows DSC plots obtained with pin-hole crucibles, at ambient pressure in the case of STA and at different pressures in the case of DSC. At the lowest pressures, both on STA and on DSC, the two dehydration

Fig. 1 TG and DTG plots obtained with open (a) and pin-hole (b) crucibles



processes appear quite well separated. In these cases, the separation is helped by the water vapor self generated atmosphere. But it can also be observed that, when increasing the pressure, the combined effect of the pressure and the self generated water atmosphere leads to a very different behavior than the observed with open crucibles. Particularly, at pressures over 10 bar, a very sharp peak appears at 154 °C. The pressure effect on the peak temperature of this process, although small in any case, is more important at pressures lower than 34 bar. Other peak, but in this case a small one, appears at 8 and 10 bar and temperature about 177 °C. Moreover, an incipient peak centered at 173 °C seems to appear at 10 bar, as can be observed with more detail in Fig. 4. It is possible that this event increases with pressure so that, at 16 bar, all these three peaks are masked by an overall event, which is shifted to higher temperatures when increasing pressure. A small event centered at 167 °C becomes evident at pressures of 16 bar and higher. The highest temperature endotherm, which may in principle be related to the second dehydration step observed at atmospheric pressure, presents a clear asymmetry and its location, on the temperature axis, is pressure dependent up to 50 bar. The shape of

this peak is very unusual, nearly trapezoidal, especially at high pressures. The asymmetry of this peak was attributed to the self generated water vapor (pin-hole) effect [17]. Nevertheless, the results presented here indicate that some important asymmetry results from pressure application, even with open crucibles. Despite this, the asymmetry produced by the pin-hole effect is more notorious and does not appear to be affected by the pressure. However, the pressure effect on the pin-hole samples consists in shifting the asymmetric peak to higher temperatures so that, at 34 bar, that peak becomes fully separated from overlapping processes. The shape of this peak at pressures of 34 bar and above is nearly trapezoidal. This shape suggests that the transformation associated to the endotherm is prevented by the high pressure until a critical temperature, T_c (which depends on the pressure), is reached. Once the critical temperature is reached, the process is triggered. Any further increase of temperature produces an acceleration of the process. The process ends sharply when the conversion is completed, in a way similar to evaporation-like processes [18]. It is also observed that the broadness of this peak diminishes when increasing the pressure up to 50 bar. It is a consequence of the blocking effect of pressure: the higher

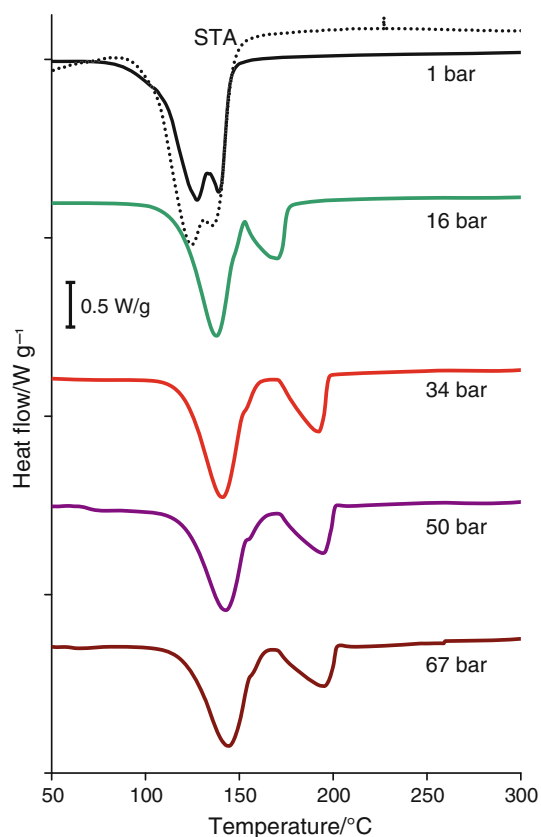


Fig. 2 Overlay of gypsum DSC curves obtained with open crucibles in STA at atmospheric pressure and in DSC at 1, 16, 34, 50, and 67 bar

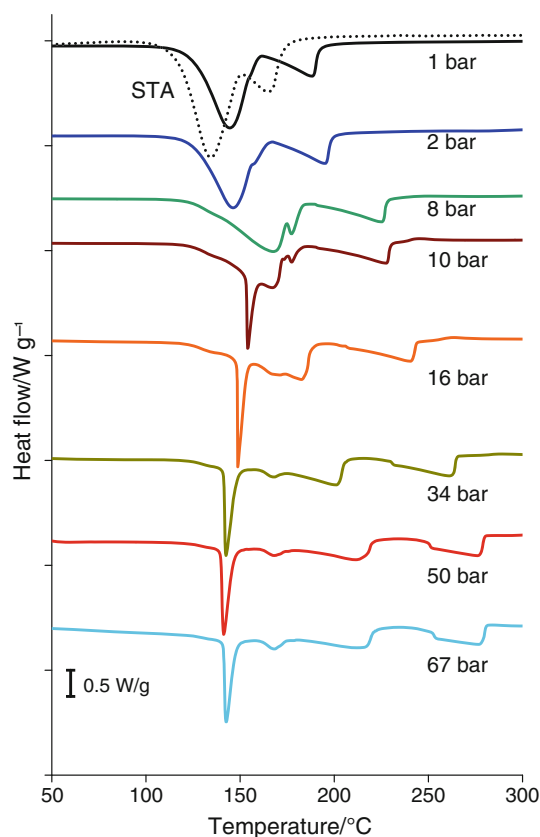


Fig. 3 DSC plots obtained with pin-hole crucibles, at ambient pressure in the case of STA and at different pressures in the case of DSC

Table 1 Values of enthalpy and area percent of the dehydration peaks obtained from the DSC experiments at different pressures with open crucibles

Pressure/bar	Area/%		Enthalpy/J g ⁻¹	
	Peak 1	Peak 2	Peak 1	Peak 2
1	73	27	396.6	147
16	69	31	357.2	163.2
34	75	25	339.7	115.3
50	74	26	300.1	105.9
67	75	25	305.1	101.1

the pressure, the higher T_c , but the higher the temperature (above T_c), the higher the reaction rate. Nevertheless, no further effect of pressure is observed above 50 bar. In order to find out if some of the low temperature processes are reversible or not, two additional experiments, consisting of heating ramps up to specific temperatures (157 and 180 °C) and followed by cooling ramps, were performed with fresh samples at 34 bar. Figure 5 shows how the peaks at 141 and 167 °C, and a small shoulder at 134 °C, do not appear in the corresponding cooling ramps. It means that these

processes are not reversible under these isobaric experimental conditions, where the evolved water vapor is swept by a nitrogen purge.

The sample initially heated up to 157 °C and then cooled to 60 °C was subjected to a new heating experiment in the full range of temperature. For comparison, this re-scan trace is plotted on Fig. 5 along with a scan of a fresh sample, obtained at the same pressure of 34 bar. A quick comparison of both traces shows that, as expected, the 141 °C peak and the 134 °C shoulder do not appear on the re-scan trace. Nevertheless, the overlapping peaks in 150–200 °C range appear clearly diminished, ending at lower temperature. This is an indication that these processes took place in part during the first scan, that is, at temperatures lower than 157 °C. On the other hand, the highest temperature peak remains almost unaltered, but slightly smaller. Since this well defined peak appears at temperatures well above than the other processes, it does not seem likely that part of the dehydration process represented by this peak took place during the first scan. However, the small decrease of that peak could be related to disorder in the lattice of pre-heated gypsum samples [19].

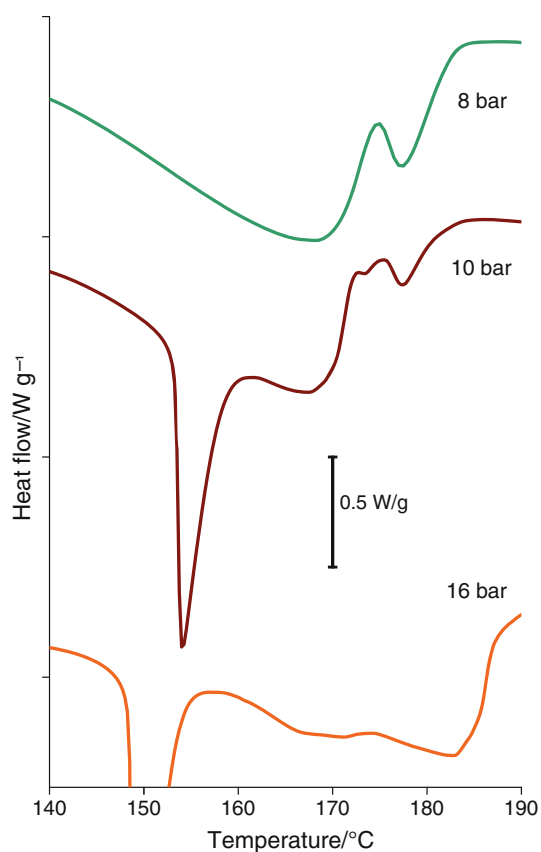


Fig. 4 Detail of DSC plots obtained with pin-hole crucibles, at 8, 10, and 16 bar

After the first heating, a small exotherm appears on cooling at about 80 °C, and its corresponding endotherm appears on the subsequent heating step at about 95 °C. These peaks indicate the presence of a crystalline polymer modifier of the plaster. The fact that no melting nor cold crystallization was observed during the first scan suggests that, during the preparation of plaster of Paris, the polymer was dissolved and intimately dispersed on the gypsum matrix. Thus, the first heating ramp would facilitate the drying and aggregation of the polymer particles which would crystallize during the cooling step. The enthalpy values observed at high pressures with pin-hole crucibles are similar to those measured for full dehydration at 1 bar. Specifically, the overall areas of DSC peaks observed at 1 and 67 bar on Fig. 3 were about 580 and 550 J g⁻¹, respectively. It suggests that most of the enthalpy changes are associated to dehydration processes. A comparison of the peak areas obtained at 67 bar, with open crucibles and pin-hole reveals that the areas of the highest temperature peaks (195 °C with open crucibles and 280 °C with pin-hole) is practically the same. It suggests that both peaks correspond to the same process, probably a subhydrate-anhydrite transformation. On the other hand, the overall area of the multiple peaks observed in the 120–240 °C

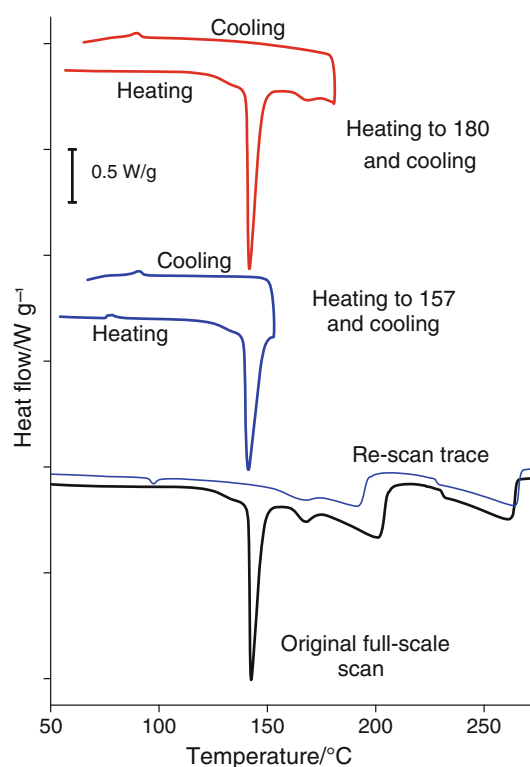


Fig. 5 DSC scans, stopped at specific temperatures, and re-scan of the sample preheated to 157 °C in the full range of temperature, at 34 bar

range for the pin-hole sample is similar to that of the low temperature peak observed with open crucibles at the same pressure of 67 bar. It seems that the change from dihydrate to subhydrates is a complex process, composed of overlapping single processes. The combined effect of self generated water vapor with pressurized nitrogen affects differently to each of the overlapping processes and originates new transformations, resulting in a neat separation of the peaks. Particularly, there is a peak at 154 °C in the 10 bar curve. This peak shifts to about 142 for higher pressures. This process is not observed for pressures lower than 10 bar. It means that 10 bar is a critical pressure for the predominance of this process over the other competitive processes. There is also a small shoulder on the left side of this peak that can be attributed to free water absorbed by the polymer modifier. At ambient pressure and with open crucibles this peak appears at about 90 °C on both DSC and DTG curves. Only with these data, it is not possible to assign the thermal changes to any specific transformation between the different hydrates. Therefore, a structural investigation was done on samples obtained by PDSC at specific temperatures. Since the amounts of sample used in the previous tests, although optimal for measuring DSC tests, were too small for XRD analysis, an additional set of experiments was done with the aim of

obtaining samples for XRD. Since these new experimental conditions are not optimal for DSC, the resulting plots, shown in Fig. 6, cannot be taken as accurate quantitative measurements of heat flow. Nevertheless, these new tests clearly inform of the thermal processes experienced by the samples to be analyzed by XRD. In fact, although the DSC curves obtained with big and small amounts of sample are similar in shape, the ranges of temperature at which each endotherm appears and the relative extent of some processes clearly depend on the sample size, type of container and compactness of the sample. For example, the relative areas of the 137 and 155 °C endotherms differ from one to other experiment. The only difference in sample preparation came from the variability associated to manual packing, which implied manual folding in aluminum foil and manual filling and compaction. Figure 7 shows the XRD spectra obtained from a fresh sample and the samples subjected to the DSC scans indicated in Fig. 6. Presence of silica was observed in all the spectra and was not affected by the thermal treatments. It is a common additive in some commercial brands of plaster of Paris. Different structures corresponding to the general formula of $\text{CaSO}_4 \cdot \text{XH}_2\text{O}$ were identified, as summarized in Table 2. It has mentioned that while assignation anhydrite and gypsum does not represent any problem, it is difficult to distinguish between different subhydrates. The intensities at 11.7 theta angle are observed to vary with the treatment temperature. This band is assigned to dihydrate and its intensity decreases when increasing the treatment temperature. According to Table 2, the small amount of anhydrite present in the fresh sample disappears upon heating to 146 °C. At the same time, two hemihydrates appear. It means that the 137 °C endotherm basically corresponds to dehydration of a part of the dihydrate to form α and β $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. The small amount of anhydrite observed in the fresh sample was rehydrated to hemihydrate due to the combined effect of

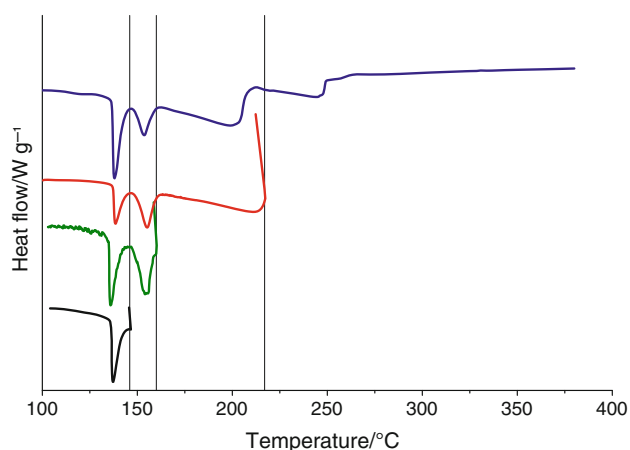


Fig. 6 DSC plots obtained at 67 bar with samples of about 200 mg packed in aluminum foil

pressure and self generated vapor of water. The phases observed after heating to 160 °C were $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 0.662\text{H}_2\text{O}$. Thus, the 155 °C endotherm corresponds to dehydration of another part of the dihydrate to form $\text{CaSO}_4 \cdot 0.662\text{H}_2\text{O}$. The $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ present at the beginning of this process was simultaneously rehydrated to the same subhydrate form, $\text{CaSO}_4 \cdot 0.662\text{H}_2\text{O}$. After heating to 217 °C, only two structures were detected: anhydrite and $\text{CaSO}_4 \cdot 0.62\text{H}_2\text{O}$. The corresponding endotherm spans from 160 to 217 °C and represents dehydration of the dihydrate and subhydrate present at the beginning of the process. The presence of some subhydrate after heating up to 380 °C was unexpected. It probably results from partial rehydration of anhydrite with the remaining water vapor, which would be represented by the small exotherm observed at 265 °C in Fig. 6, or from spontaneous rehydration when

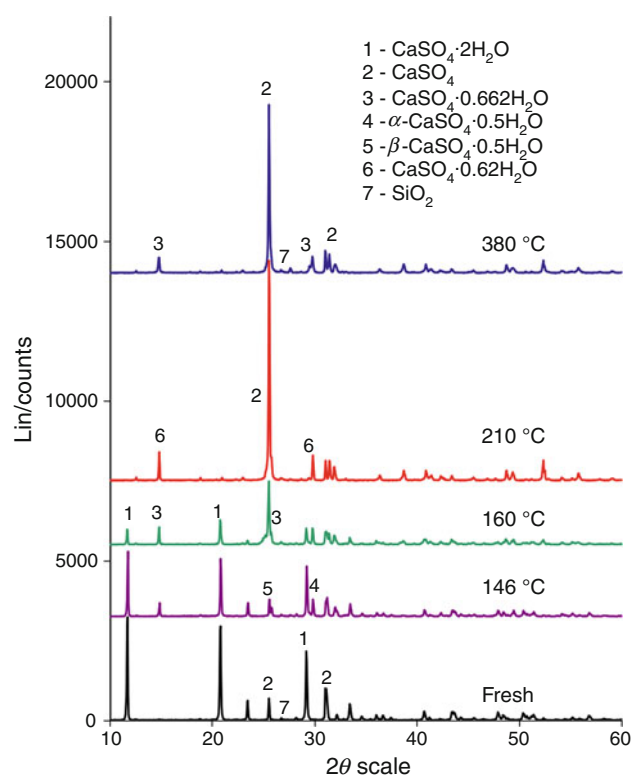


Fig. 7 XRD spectra obtained from a fresh sample and from samples preheated to the indicated temperatures

Table 2 Structures identified by X-ray diffraction from samples which were heated up to the indicated temperature and then cooled. Heating and cooling was done at a 67 bar pressure

Fresh	×	×		
146 °C	×			×
160 °C		×	×	
210 °C		×		×
380 °C		×	×	

exposed to ambient for XRD analysis. The results presented here demonstrate how the combined effect of pressure and self generated vapor of water affects differently to each of the overlapping processes and originates new transformations. In addition, PDSC can be used to obtain a neat separation of the overlapping processes. Nevertheless, according to other reports, there is still some uncertainty with respect to the type of phases produced in each single process [15]. Apart from the pressure and thermal program there are other factors, such as the sample size, type of container and compactness of the sample, which affect the extent and the range of temperature at which each single process takes place. The influence of these factors seems to be related to the amount of self generated vapor of water retained in contact with the sample.

Conclusions

A complete separation of dehydration processes of gypsum can be obtained by increasing the pressure. The enthalpies of the processes decrease when increasing the pressure with open crucibles. When using pin-hole crucibles, the self generated vapor of water combined with the applied pressure seriously affects the structure of calcium sulfate hydrates, especially at pressures above 2 bar.

A neat separation of several transformation involved in dehydration of gypsum was obtained by combining PDSC with pin-hole crucibles. Several transformations were identified through XRD analysis of samples treated in a PDSC. Nevertheless, there is still some uncertainty with respect to the type of phases produced in each single process.

The sample size, type of container, and compactness of the sample clearly affect the range of temperatures at which each process takes place at a given pressure and the relative extent of some processes. Consequently, the heat flow data of the thermal treatment of sample to be analyzed by XRD are needed to correlate thermal and structural transformations.

The use of PDSC may provide an interesting insight for the study of dehydration processes and structural changes of minerals.

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