

In situ IR spectroscopic and thermogravimetric study of the dehydration of gypsum

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Abstract

The dehydration of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has been studied, at negligible water vapour pressure, by *in situ* infrared (IR) spectroscopy and by thermogravimetry to determine whether intermediate phases ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$) exist, other than the hemihydrate with $n=0.5$, and also to compare the mechanism of the dehydration process when measured by two techniques with very different correlation lengths. Thermogravimetry shows an apparently continuous water loss with an activation energy of $90.3 \text{ kJ} \cdot \text{mol}^{-1}$, with no changes in the activation energy as a function of the degree of dehydration. IR spectroscopy on the other hand, clearly shows the existence of three discrete phases, gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, hemihydrate $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\gamma\text{-CaSO}_4$, with nucleation of each successive phase as dehydration proceeds. There is no evidence to suggest the presence of phases with any intermediate water content.

KEYWORDS: gypsum, dehydration, infrared spectroscopy, thermogravimetry.

Introduction

DESPITE many previous studies of the dehydration and rehydration of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (see e.g. Lager *et al.*, 1984) considerable uncertainty exists on a number of points:

(a) Are there any intermediate phases, $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$, other than the hemihydrate where $n=0.5$? Although such phases have been proposed, and studied by diffraction methods (Abriel, 1983; Abriel *et al.*, 1988; Bushuev and Borisov, 1982), arguments based on H_2O – H_2O distances do not favour the existence of 'hemihydrates with excess H_2O ' (Lager *et al.*, 1984). Furthermore, McConnell *et al.* (1987) find no such intermediate phases, even at the high water pressures which Abriel *et al.* (1988) suggest are needed for their stabilization. However, we note that diffraction methods with their relatively long correlation length may also not be the ideal way of studying the local structural changes associated with dehydration.

(b) What is the mechanism of the dehydration sequence gypsum–hemihydrate– $\gamma\text{-CaSO}_4$? Typically, the dehydration process is studied by thermogravimetry and the dehydration mechanism is

determined from the rate law for water loss (see e.g. Ball and Norwood, 1969; Ball and Urie, 1970). Such methods have their shortcomings, due to problems such as the possible presence of intergranular and surface water, to the empirical nature of the correlation between rate law and reaction mechanism, and also due to the fact that thermogravimetry is a macroscopic technique which cannot determine the mechanism at a local level.

(c) The possibility of rehydration of the dehydrated forms and the difficulty of determining the water content introduces uncertainties in structural work at room temperature, and has led to a number of controversial studies of phases with water contents up to 0.8 per formula unit (Abriel, 1983; Bushuev and Borisov, 1982).

High-temperature studies are therefore necessary, and the present study describes *in situ* experiments of the dehydration sequence of gypsum heated *in vacuo* in an infrared (IR) spectrometer. IR spectroscopy is especially suitable in this context, being both very sensitive to the water content as well as providing some qualitative structural information on a local scale. For comparison, a

parallel study by thermogravimetric analysis of the kinetics of water loss was carried out. Although the experimental conditions cannot be made identical to those in the IR experiment, the thermogravimetric study provides a macroscopic view of the dehydration process as well as providing kinetic data which can be used to calculate the empirical activation energy at incremental steps of H₂O loss.

Thermogravimetric analysis

One of the aims of the thermogravimetric study was to test whether any discontinuities in the dehydration process could be detected by changes in the activation energy through the dehydration sequence gypsum-hemihydrate- γ -CaSO₄.

The thermogravimetric study was carried out in a Stanton-Redcroft TG761 balance, an important feature of which is the ability to heat the sample to the desired isothermal run temperature very quickly (990°C per minute), before any dehydration takes place. The fractional weight loss was measured as a function of temperature and time between 63°C and 106°C in a dry N₂ atmosphere with a constant gas flow rate. Dehydration is extremely slow at temperatures below 70°C but is very rapid at temperatures above 100°C. The gypsum sample used was a ground fragment of a large natural single crystal.

A method of determining the activation energy E_a of incremental steps in the dehydration process was used to identify any such discontinuities. The method (Giampaolo and Putnis, 1989) takes the general rate equation

$$\frac{dy}{dt} = k \cdot f(y), \quad (1)$$

where y is the fraction of the total H₂O lost and $f(y)$ is a function dependent on the mechanism, and considers t rather than y as the dependent variable

$$dt = k^{-1} \cdot f^{-1}(y)dy. \quad (2)$$

Hence the time t_y for a given fractional dehydration $y = Y$ is

$$t_Y = k^{-1} \int_{y=0}^{y=Y} f^{-1}(y)dy. \quad (3)$$

The output from the thermogravimetric balance gives the weight loss as a function of time from which values of t_Y can be determined for a series of temperatures. If $f(y)$ does not change over the temperature range studied, the integral has a constant numerical value, and

$$t_Y \propto A^{-1} \exp(E_a/RT). \quad (4)$$

A plot of $\ln t_Y$ against $1/T$ is linear with slope E_a/R if E_a and A are independent of T . This method allows the determination of E_a independently of the choice of the rate equation.

From the thermogravimetric data for isothermal dehydration at six different temperatures, the time T_Y for eight increments of the fractional weight loss y from 0.1–0.2, 0.2–0.3, 0.3–0.4 . . . up to 0.8–0.9 was determined. Fig. 1 shows the Arrhenius plots for each increment, from which the activation energy as a function of the dehydration process was evaluated.

The conclusion which is apparent from this plot is that there is no significant change in the empirical activation energy throughout the dehydration process at temperatures between 63°C and 106°C, and that from this macroscopic point of view the process appears to be completely continuous. The value of E_a from the average slope of the plots is found to be 90.3 kJ.mol⁻¹ (21.5 kcal.mol⁻¹). This value is very similar to the value obtained by Ball and Norwood (1969) [\sim 23 kcal mol⁻¹], which they attribute to a phase-boundary-controlled reaction (i.e. that the rate controlling step in the process is the migration of the hemihydrate-gypsum interface).

From powder X-ray diffractometry carried out immediately after the experiments, the final dehydration product was found to be γ -CaSO₄ at all temperatures, although diffraction peaks due to hemihydrate were already present, confirming the rapid rehydration. Assuming that during the dehydration sequence the sample is likely to have been a phase mixture of gypsum + hemihydrate + γ -CaSO₄, we conclude that under the conditions of this experiment the dehydration of gypsum and of hemihydrate proceeds by a similar mechanism with a similar activation energy. The macroscopic nature of the thermogravimetric method averages out the contributions from different mechanisms, and in the presence of a phase mixture could not distinguish between a continuous and discontinuous process, even when measured at small increments of water loss. The use of thermogravimetry to characterise the H₂O content of partially dehydrated CaSO₄. n H₂O cannot be used to infer the phase(s) present.

Infrared spectroscopy

There have been a number of IR studies of the dehydration products of gypsum. Of particular interest in our context is the work of Bensted and Prakash (1968) who investigated the possibility of the existence of two forms of hemihydrate (α and β), but concluded that there are only three dehydration products of the dehydration of gyp-

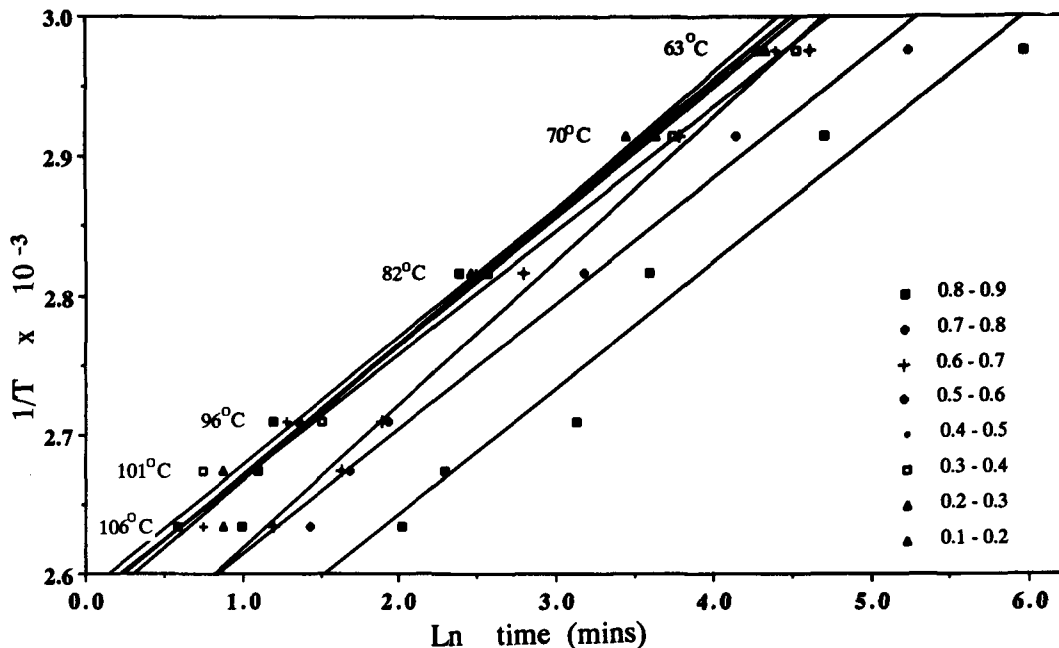


Fig. 1. Plot of \ln time ($t_{\Delta y}$ in minutes) against temperature ($1/T$ in Kelvins), where $t_{\Delta y}$ is the time taken for a particular interval Δy of the fraction dehydrated. The slopes of the plots for each dehydration interval (indicated by the symbols in the legend) were determined by linear regression and used to determine the activation energy (Eqn. 4). The virtually constant slopes for each of the eight intervals measured (0.1–0.2, 0.2–0.3, etc.) indicates that the activation energy does not change significantly as a function of the fraction of water lost.

sum, namely hemihydrate, soluble (γ), and insoluble (α) anhydrite. They listed the IR frequencies of all three forms in the range from 3600cm^{-1} to 650cm^{-1} and we use these data, together with those by Seidl *et al.* (1969) in the range down to 400cm^{-1} for the identification of the phases present in our experiments.

Powder IR spectra were recorded in the range from 4000 to 500cm^{-1} with 2cm^{-1} resolution, on a Bruker IFS 113v FTIR spectrometer using the KBr disc technique. Samples were heated in a resistance furnace mounted inside the evacuated sample chamber, and the temperature controlled by a thermocouple placed directly next to the sample. IR spectra (128 scans) were collected during the dehydration process at a number of different temperatures in the range 50 to 80°C . As at high temperatures the dehydration was too fast to be followed, we used a slow continuous heating procedure to be able to measure all levels of dehydration in one sample.

The IR spectra were followed *in situ* by observing the changes in three spectral regions: (i) the O–H \cdots O stretching vibrations in the range 3800 to 3000cm^{-1} , (ii) the in plane O–H \cdots O bending vibrations in the range 1800 to 1500cm^{-1} , and

(iii) the ν_4 bending vibration of the SO_4 tetrahedron in the range 700 to 550cm^{-1} . The assignments of the bands are summarized in Farmer (1974).

Fig. 2 shows the change in the spectral region from 3800 to 3000cm^{-1} during the dehydration. The upper spectrum (Fig. 2a) is of gypsum at room temperature, showing the two strong bands at 3406 and 3556cm^{-1} and a few weak bands and shoulders. During dehydration the intensities of the $\nu_{\text{OH, gypsum}}$ bands decrease strongly. Concomitantly, the $\nu_{\text{OH, hemihydrate}}$ bands (Bensted and Prakash, 1968) appear, first as a high-energy shoulder to the high-energy $\nu_{\text{OH, gypsum}}$ band (Fig. 2b), then as distinct bands. As the low-energy $\nu_{\text{OH, hemihydrate}}$ band at 3552cm^{-1} coincides with the high-energy gypsum band, its appearance during dehydration can initially only be inferred from the smaller intensity decrease of the high-energy $\nu_{\text{OH, gypsum}}$ band compared to the low-energy $\nu_{\text{OH, gypsum}}$ band. Spectra 2b–2d may be interpreted as a phase mixture of gypsum + hemihydrate, although this interpretation will be more clearly justified by considering the other spectral ranges in more detail. In spectra 2e and 2f no characteristic gypsum bands can be observed. Both $\nu_{\text{OH, hemi-}}$

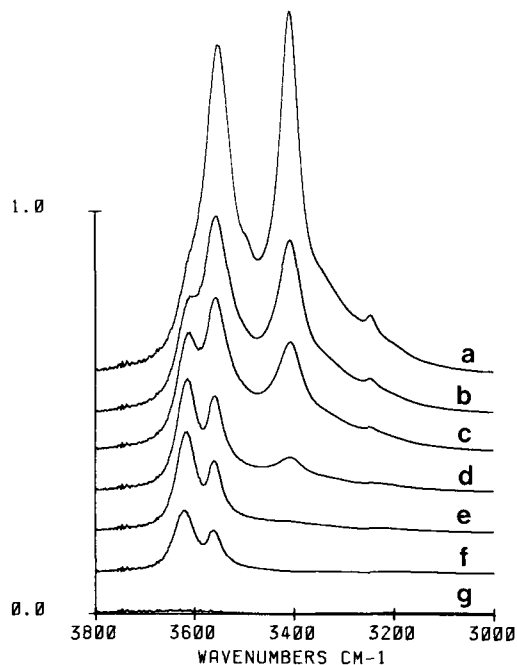


FIG. 2. Sequence of IR spectra showing the O-H...O stretching region in the range 3800 to 3000 cm^{-1} during the dehydration of gypsum. (a) gypsum, (b)–(d) a mixture of gypsum + hemihydrate. The disappearance of the band at 3406 cm^{-1} indicates that no gypsum is present, and the spectrum is due to the hemihydrate only.

hydrate bands lose intensity at about the same rate during further dehydration, until no more bands related to OH-stretching vibrations can be observed.

The bands related to the bending vibration of the O-H...O group are shown in Fig. 3. The δ_{OH} bands are not overlapping and are therefore suited to a more detailed analysis. After subtraction of a linear background, using the software supplied by Bruker, we used a program written by U. Bismayer, Hannover, to determine the frequency of the absorption maxima, the height of the band, and the full width at half maximum (FWHM). This was done by a least squares fit of two bands to spectra 3a–d and of one band to spectra 3e and 3f. The shape of the band was constrained to be Lorentzian. The results are given in Table 1. There are small shifts in the frequencies of the bands during dehydration, due to the elevated temperatures ($\sim 373\text{ K}$) at which the spectra were measured. They agree with those observed by Seidl *et al.* (1969). We observed only a slight increase of the FWHM from $18 \pm 1\text{ cm}^{-1}$ for the low-energy δ_{OH} in gypsum to $20 \pm 2\text{ cm}^{-1}$

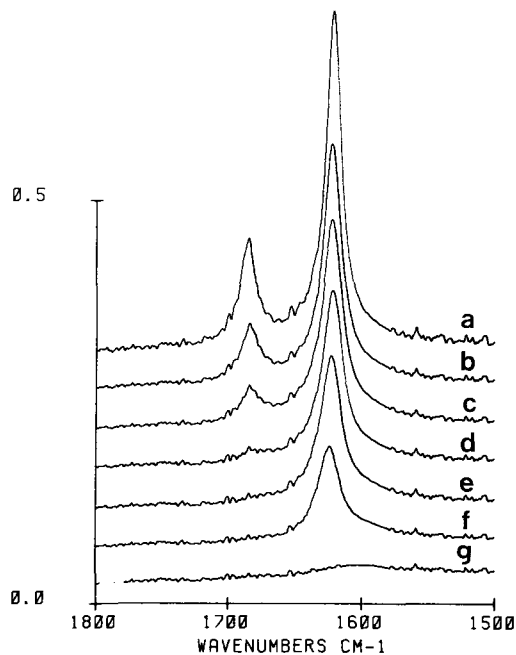


FIG. 3. IR spectra of the bending vibration of the O-H...O group in the range 1800 to 1500 cm^{-1} during the same dehydration sequence (a–g) as in Fig. 2: (a) gypsum; (b)–(e) gypsum + hemihydrate, with decreasing amounts of gypsum; (f) hemihydrate + minor $\gamma\text{-CaSO}_4$ (by comparison with Fig. 4); (g) virtually all $\gamma\text{-CaSO}_4$. The position and FWHM of these bands tabulated in Table 1 shows that there are no progressive changes in the structural environment of the OH groups during dehydration.

TABLE 1. Position (ν), full width at half maximum (FWHM) and area of the two δ_{OH} bending vibrations during a dehydration sequence. R-value of fits is between 3.5–6.5%. The labels a–f refer to the spectra in Fig. 3.

	$\delta_{\text{OH I}}$			$\delta_{\text{OH II}}$		
	ν cm^{-1}	FWHM cm^{-1}	Area arb.units	ν cm^{-1}	FWHM cm^{-1}	Area arb.units
a	1685	17.8	3.11	1621	15.6	9.48
b	1684	16.1	1.81	1622	15.6	7.65
c	1682	17.5	1.23	1622	17.1	7.10
d	1681	18.02	0.48	1622	18.0	6.24
e				1622	22.75	6.92
f				1624	19.89	3.77

for the δ_{OH} vibration in the spectra where only one δ_{OH} vibration is observed. This small increase is also caused by the elevated sample temperatures. Thus we see no evidence, during dehydration, for a progressive structural change involving the formation of hydrogen bonds with different strength, as this should result in broad-

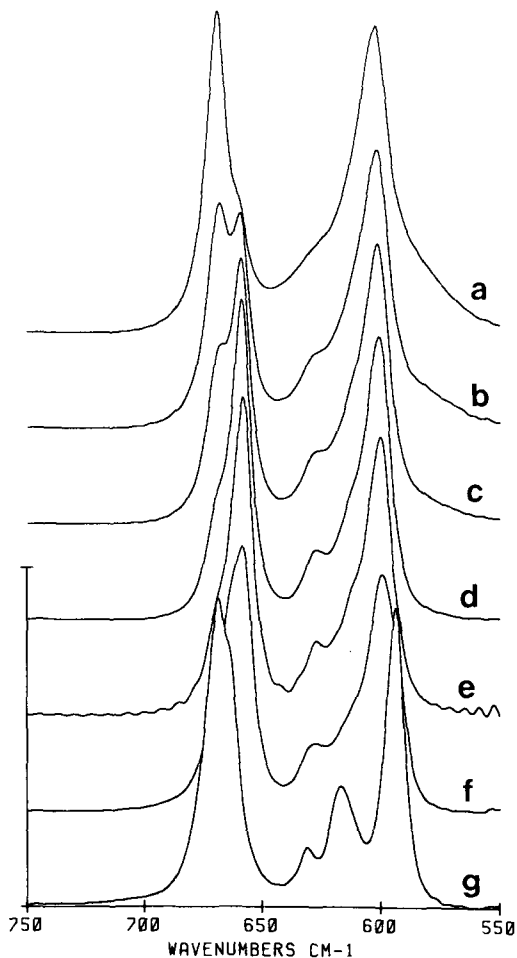


FIG. 4. The changes in the IR spectra due to the ν_4 (bending) vibration of the SO_4 tetrahedron during the dehydration sequence (a-g) as in Figs 2 and 3: (a) gypsum at room temperature; (b)-(d) a mixture of gypsum + hemihydrate; (e) hemihydrate; (e)-(f) a mixture of hemihydrate + $\gamma\text{-CaSO}_4$; and (g) virtually all $\gamma\text{-CaSO}_4$.

ening and splitting of bands. This further reinforces the interpretation of distinct structural states for the two hydrated phases, gypsum and hemihydrate.

In Fig. 4, the changes of the frequencies related to the ν_4 (bending) vibration of the SO_4 tetrahedron are shown. Spectrum 4a, of gypsum at room temperature, shows two main bands at 602 and 668 cm^{-1} . Spectrum 4e displays the bands characteristic for hemihydrate at 658 and 600 cm^{-1} . Spectra 4b-d shows bands belonging to a mixture of gypsum and hemihydrate. Clearly the intensities of bands characteristic of hemihydrate

rate increase during the dehydration process. With the exception of a weak low-energy shoulder at the 668 cm^{-1} band, spectrum 4g shows no bands characteristic of hemihydrate, but only those characteristic of $\gamma\text{-CaSO}_4$ (at 668 and 594 cm^{-1} , with minor bands at 631 and 616 cm^{-1}), while in spectrum 4f weak shoulders and a noted asymmetry of the low-energy hemihydrate band indicate the presence of a small amount of $\gamma\text{-CaSO}_4$. Spectra 4e and 4f therefore show the difference between IR spectra taken from a mixture of hemihydrate + gypsum, and hemihydrate + $\gamma\text{-CaSO}_4$ respectively, where both the latter components are just present in small concentrations. This now allows us to interpret spectra 3e and 3f in the same way, as shown in the caption to Fig. 3.

Discussion

Seidl *et al.* (1969) showed by isotopic dilution that all water molecules in gypsum are equivalent and asymmetric. They therefore concluded that the complex spectrum of gypsum in the OH-stretching region is due to vibrational coupling between neighbouring water molecules. By the same argument the two δ_{OH} vibrations in gypsum are explained, as without vibrational coupling only one δ_{OH} band should be observed. We observe only two bands related to the stretching vibrations of water and one δ_{OH} band in hemihydrate. We therefore conclude that there is no vibrational coupling in hemihydrate as, due to the dehydration, the remaining water molecules are sufficiently isolated to prevent this. It is therefore not possible to correlate the water contents to the intensity of the OH bands in a straightforward way, at least not for gypsum-hemihydrate mixtures.

Using our observations of the changes in all three parts of the spectra, we conclude that the first stage of dehydration is from gypsum to hemihydrate. Only very minor amounts of $\gamma\text{-CaSO}_4$, if any, are formed at this stage, as we did not observe shoulders at the bands characteristic of gypsum and hemihydrate which would indicate the presence of low-intensity $\gamma\text{-CaSO}_4$ bands. We cannot give a quantitative estimate, but according to Morris (1963) who determined the ratio of both phases in hemihydrate-gypsum mixtures by IR spectroscopy, the changes in the hemihydrate-gypsum spectra are large enough to detect amounts of a few percent of each substance. As the $\gamma\text{-CaSO}_4$ spectrum differs markedly from the gypsum and hemihydrate spectra, we would expect that we should be able to detect the presence of $\gamma\text{-CaSO}_4$ due to changes in the band profiles, if during the first stage of the dehydration

there was more than a minor amount of γ -CaSO₄ present.

In spectrum 4e, we only note two weak shoulders at the high-energy sides of the two main bands characteristic of hemihydrate, which indicate that minor amounts of gypsum are still present. This could not be noted in spectrum 2e, where we did not see any remains of the low-energy major OH stretching band belonging to gypsum. The bending vibrations of the SO₄ tetrahedron are more sensitive to the gypsum-hemihydrate structural change than the OH-stretching region.

The sequence of spectra in Fig. 4 clearly shows that during the dehydration process we first have a mixture of gypsum + hemihydrate, and with further dehydration, a mixture of hemihydrate + γ -CaSO₄. Furthermore the one bending vibration (at 1622 cm⁻¹) common to both gypsum and hemihydrate does not change its position or FWHM significantly (Fig. 3 and Table 1) nor do we see any splitting of the OH stretching vibration when hemihydrate is dehydrated (Fig. 2). We therefore conclude that there is only one kind of hemihydrate, i.e. we could not confirm the existence of hemihydrates with more or less than 0.5 H₂O per formula unit. This asserts our earlier suggestion that thermogravimetry is not a suitable method for the analysis of the dehydration of gypsum.

One further, and vital, parameter which controls the kinetics of the dehydration and may also determine the decomposition products, is the partial pressure of water vapour. In the present experiments the water vapour pressure was negligible in both cases, the TG experiments being carried out in dry nitrogen and the IR experiments in a continuously pumped vacuum using a dry KBr disc. Any water in the KBr disc would have been immediately obvious in the IR spectrum. To check further that the TG and IR data are comparable, a KBr disc containing gypsum prepared as for IR spectroscopy was heated in the thermogravimetric balance. The water loss followed the same kinetics as in Fig. 1, confirming that differences in specimen preparation have no effect on the dehydration mechanism in the two experiments.

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