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Anion water in gypsum ($CaSO_4 \cdot 2H_2O$) and hemihydrate ($CaSO_4 \cdot 1/2H_2O$)

Pradip K. Mandal*, Tanuj K. Mandal

National Thermal Power Corporation Limited, Research and Development Centre, A-8A, Sector-24, Noida 201301, India

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Abstract

The bonding nature of water in gypsum, $CaSO_4 \cdot 2H_2O$, and hemihydrate, $CaSO_4 \cdot 1/2H_2O$, was suggested by characteristic absorption bands of water and sulphate ions. The infrared spectral data indicate the presence of anion water in gypsum and hemihydrate through hydrogen bonding. Negative shifting of bending vibration of SO_4 ion and lowering and broadening of the O – H stretching vibration at around 3600 cm^{-1} indicate the presence of both anion water and hydrogen bonding in gypsum and hemihydrate © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Gypsum; Hemihydrate; Anhydrite; X-ray diffraction; Infrared spectroscopy

1. Introduction

There is a considerable research interest in the study of structure and coordination behaviour of water molecules in gypsum (calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$) and hemihydrate (plaster of Paris, $CaSO_4 \cdot 1/2H_2O$).

A wide range of opinions concerning the dehydration of gypsum and various ideas relating to its mechanism are well known [1–15].

The chemistry of the gypsum transformation products on heating is still, despite extensive work, not entirely agreed upon. It is claimed [5] that heating gypsum below 100 °C gives rise to limiting value of weight loss around that of the hemihydrate formation indifferent of the length of heating time. Calcination above 100 °C causes a continuous loss in weight as the time is prolonged, leading to anhydrite ($CaSO_4$). Hamad [14] has reported the presence of molecular hydrogen and hydrogen-bonded water molecules in the gypsum and hemihydrate structures. There has been considerable controversy on the bonding of water in gypsum and hemihydrate. The crystal structure of gypsum was determined by X-ray data by several workers [16–19] and it was suggested that the water molecules in gypsum are asymmetrical [16]. Some suggested that gypsum has a layer structure [17]. However, the presence of anion water in gypsum has not been discussed so far. The water, which is coordinated through anion of a compound via hydrogen bonding, is called anion water [20]. Due to presence of anion water, the water molecule is held strongly and difficult to remove from the parent compound due to which more heat energy is required to release this water molecule. In case of gypsum, the anion water is removed through heating nearly by 350 °C.

The present paper describes the hitherto unknown incidence of presence of anion water in gypsum and hemihydrate. These are characterised by X-ray diffraction and infrared spectroscopy.

2. Experimental

A gypsum sample ($CaSO_4 \cdot 2H_2O$, 98% pure) was used for this investigation. The sample of hemihydrate was prepared by following the published procedure [3,15]. The impurities present in the gypsum sample were determined by XRF analysis: SiO_2, 0.08%, Al_2O_3, 0.12%, MgO, 0.09% and Fe_2O_3, 0.09%. The anhydrite was prepared by heating the gypsum at 350 °C for 10 h.

The assessment of formation of phases was carried out by determining the percentage weight loss and X-ray analysis. X-ray analysis was carried out using a diffractometer with CuK_α radiation (at 2θ scanning speed of 1°/min) from 5° to 85° 2θ. Equipment used was Rigaku Dmax RU 200, 12 kW,

* Corresponding author. Tel.: +91-8-441-0582; fax: +91-8-441-0311.
E-mail address: pkm@ntpcrd.ernet.in (P.K. Mandal).

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equipped with graphite diffracted beam monochromator. The accelerating voltage was 50 kV and the current was 100 mA (5 kW).

The infrared spectra were recorded in a Perkin-Elmer Model-237 spectrometer using the KBR disc technique. Each spectrum was calibrated by polystyrene film.

3. Results and discussion

On heating the gypsum sample at 90 °C for 10 h, a weight loss value of about 15.10 g is observed. It is related to the evolution of 3/2 molecules of water from gypsum sample. At 90 °C, dehydration of gypsum does not proceed beyond the hemihydrate whatever is the duration of heating. This observation indicates that after heating at 90 °C for 10 h, the residual water molecules in hemihydrate are strongly held. The loosely held 3/2 water molecules are completely driven off at this temperature. Heating at 350 °C for 10 h gives complete removal of strongly held 1/2 molecules of water from hemihydrate, $CaSO_4 \cdot 1/2H_2O$. This indicates that gypsum contains two types of water molecules: one loosely held and other strongly held.

Thermal analysis data (DTA) were not able to explain the loosely and strongly held water molecules in gypsum and hemihydrate and the contribution of bonding towards the above behaviour. In the present study, the nature of bonding was explained by infrared spectral data.

The changes of crystal structure of gypsum on heating are evaluated by X-ray diffraction. The XRD data of gypsum, hemihydrate and anhydrite indicate that most of the peaks (2θ versus intensity) are different from each other. There are three major peaks at 11.59°, 20.72° and 29.11° 2θ in gypsum, 14.75°, 29.70° and 31.86° 2θ in hemihydrate and only 25.44° 2θ in anhydrite. On heating, the gypsum structure got changed [21] with elimination of 3/2 molecules of H_2O and hemihydrate is formed. At this stage, only the loosely held water molecules ($3/2H_2O$) got released with change of symmetry. The symmetry is hexagonal. On further prolonged heating, the hexagonal symmetry of hemihydrate is preserved for a long time and finally at higher temperature ($\sim$ 350 °C), the orthogonal anhydrite formed, which is evident from the XRD data of hemihydrate and anhydrite. There are greater numbers of XRD active peaks in case of gypsum and hemihydrate and which are less in case of anhydrite, indicating low degree of crystallinity and distortion of lattice. This is because of release of strongly held water molecule ($1/2H_2O$) resulting in major collapse of the structure. This was also observed by Hamad [21] by the study on the image and lattice of a dehydrated gypsum by electron microscope.

3.1. Absorption bands of water molecule [22–24]

The presence of water in a sample can be detected by its two characteristic absorption bands in the 3600–3200 cm^{-1} region and in the 1650 cm^{-1} region. It is clear from the absorption spectra of gypsum that the presence of two bands at 1680 and 1620 cm^{-1} (bending vibration) are due to the presence of two types of water molecules in gypsum. The band 1680 cm^{-1} is for loosely held water molecule, and the 1620 cm^{-1} band arises from strongly held water molecule (anion water). The hemihydrate contains only strongly held anion water and possesses the only one bending vibration at 1620 cm^{-1}. The two bands at 3400 and 3600 cm^{-1} in gypsum are assigned as O–H stretching. In the spectra of the hemihydrate, the bands are positioned at 3550 and 3600 cm^{-1}. Hydrogen bonding lowers the frequency and broadens the band in 3600 cm^{-1} region [22]. In gypsum, there are more water molecules, which help in forming more O–H···O bonds. The band 3600 cm^{-1} in hemihydrate is lowered to 3540 cm^{-1} in gypsum, and the band 3550 cm^{-1} in hemihydrate to 3400 cm^{-1} indicates the hydrogen bonding. Hemihydrate contains only one type of water molecule attached to the anion, SO_4^{2-}, by hydrogen bonding but gypsum contains two types of water molecules out of which one is attached to the anion, SO_4^{2-}, by hydrogen bonding. The unique band at 1620 cm^{-1} due to bending vibration of water molecule is present both in gypsum and hemihydrate as both contain the anion water (Table 1).

3.2. Absorption bands of the SO_4 ion [22–24]

The anion SO_4^{2-} belongs to the higher symmetry point group (T_d); on linking to a water molecule, the symmetry of SO_4^{2-} ion will be lowered [23]. In case of gypsum, $CaSO_4 \cdot 2H_2O$, the symmetry of the sulphate ion becomes

Table 1
Infrared frequencies of gypsum in various hydrated states (cm^{-1})

Material	$\nu_{2(S-O)}$	$\nu_{3(S-O)}$	$\nu_{4(S-O)}$	Probable symmetry of SO_4^{2-} group	$\nu_{(O-H)}$	$\delta_{(O-H)}$
$CaSO_4 \cdot 2H_2O$	–	1120	670	almost T_d	3540	1680
			600		3400	1620
$CaSO_4 \cdot 1/2H_2O$	490	1195	650	C_{2v}	3600	
		1110				1620
		1080	580		3550	
$CaSO_4$	510	1190	675	lower than C_{2v}	–	–
		1130	610			
		1090	595			

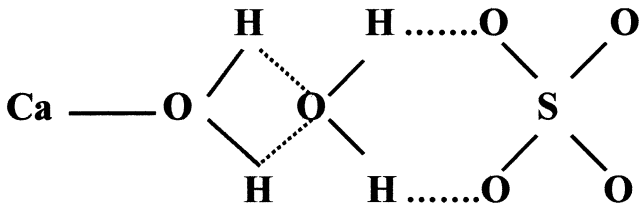

Fig. 1. Skeletal structure of gypsum showing anion water.

C_{2v}. The infrared spectra of gypsum exhibit only one stretching band (ν_3) at 1120 cm^{-1}, which is indicative of T_d symmetry. In anhydrite, three stretching bands (ν_3) in this region are clearly noticed (Table 1). This indicates that the symmetry is lowered in the case of anhydrite.

The anhydrite, hemihydrate and gypsum exhibit three (675, 610, 595 cm^{-1}), two (650, 580 cm^{-1}) and two (670, 600 cm^{-1}) bending vibrations, respectively, in the infrared spectrum. The change in the absorption pattern of bending vibration indicates certain changes in the configuration of SO_4 ion. This may be attributed to the perturbation of the sulphate ion by neighbouring H_2O molecules. The lowering of the absorption peaks from frequency 675 cm^{-1} in anhydrite to 650 cm^{-1} in hemihydrate indicates that the SO_4 ion in hemihydrate is linked through the water molecule (anion water) by hydrogen bonding. The lowering of the peak 675 cm^{-1} in anhydrite to 670 cm^{-1} in gypsum also indicates the presence of anion water. The 600 cm^{-1} peak in gypsum splits into two peaks at 610 and 595 cm^{-1} in anhydrite. This is due to lowering of symmetry from T_d to C_{2v}.

Hence, the infrared spectral studies on absorption bands of water molecules and SO_4 ion in gypsum reveal that in $CaSO_4{\cdot}2H_2O$, 3/2 molecules of water are attached to Ca atom directly and 1/2 water molecule is held to the sulphate ion by hydrogen bonding.

On the basis of the data discussed above, the skeletal structure of gypsum has been proposed and given in Fig. 1.

The studies of Pedersen and Semmingsen [16] and Cole and Lancucki [17] have shown that the symmetry of the SO_4 ion in gypsum is lowered from tetrahedron in the point group $\bar{4}3m$ (hexatetrahedral) to a sphenoid in point group $\bar{4}2m$ (tetragonal bis phenoidal). The reduced symmetry probably arises because of the different environment surrounding the two crystallographically distinct sulphate oxygens, O (I) and O (II). The symmetry-related pair of atoms oxygen (I) and oxygen (I′) is each hydrogen-bonded to two water molecules towards which they face, whereas the symmetric-related pair oxygen (II) and oxygen (II′) forms no hydrogen bonds but has close Ca^{2+} neighbours.

In the present study, also it was observed that the water molecules are asymmetric, i.e., two different types of water molecules in gypsum are present and they are designated as loosely held (3/2 H_2O) and strongly held (1/2H_2O).The attachment of two asymmetric water molecules in gypsum can be better explained by the fact that in gypsum, 3/2 molecules of water (loosely held) are attached directly to Ca atom and 1/2 molecule of water (strongly held, anion water) is bounded to the sulphate ion by hydrogen bonding (Fig. 1). On being heated, dehydration of gypsum takes place in steps, first forming $CaSO_4{\cdot}1/2H_2O$ and finally anhydrite, $CaSO_4$. Anion water is held tenaciously up to 350 °C application of heat, and causes loss of 3/2 nonhydrogen-bonded waters and finally the anion water, thus confirming the proposed structure of gypsum, $CaSO_4{\cdot}2H_2O$ (Fig. 1).

4. Conclusion

The anion water is not particularly common but certainly occurs in $CaSO_4{\cdot}2H_2O$. Such water is associated with an anion rather than with a cation by hydrogen bonding.

On heating, dehydration of calcium sulphate dihydrate ($CaSO_4{\cdot}2H_2O$) takes place in steps, first forming $CaSO_4{\cdot}1/2H_2O$ and finally anhydrous $CaSO_4$. Anion water is held tenaciously up to 350 °C. Application of heat causes successive loss of 3/2 water molecules linked to the Ca atom, and finally the anion water.

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