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Studies on treated phosphogypsum by infra-red spectroscopy

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Phosphogypsum is an important industrial byproduct which can be converted, after proper treatments, into useful building materials. Characterization of this refined material could be done by different techniques. Infra-red spectroscopy provides a quick method of identification of various forms of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ system present in the sample. Different treated samples of phosphogypsum obtained from fertilizer plants have been studied by this technique.

Infra-red spectroscopy which has been earlier known to be a powerful tool exclusively for the study of organic compounds, is now being increasingly used for studying minerals in clays and other inorganic materials. In the IR spectra of inorganic compounds, the bands of characteristic absorption are limited and broad because the molecules can not vibrate freely in a crystal. Based on earlier studies IR spectra of very vast range of naturally occurring and artificially produced inorganic materials are recorded in a number of atlases¹⁻³ which provide easy access to standard spectra of pure materials for identification of mineral phases present in unknown materials.

Exhaustive investigations during the last three decades by a number of workers⁴⁻⁶ have shown the usefulness of this technique in the elucidation of mineral phases of inorganic materials such as silicates, carbonates, sulphates, nitrates, cyanides, phosphates etc. and their composites.

Infra-red absorption spectra of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ systems have been a subject of study of a number of workers⁷. The technique provides a quick method of identification of various forms such as gypsum, hemihydrate and anhydrite. Phosphogypsum, which is an important byproduct of phosphate fertilizer industry, can be converted into useful building materials after appropriate treatment for removal of undesirable impurities.

In the present paper the IR absorption bands of treated phosphogypsum samples have been studied and their spectral characteristics used for quick identification of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ phase present in each of them.

Experimental Procedure

Four samples of phosphogypsum were obtained from fertilizer plants. These samples were given various washing and drying treatments before using them for the production of different building

materials. These treated phosphogypsum samples were collected and stored in air-tight desiccator and were marked A-D.

The IR spectra of the samples were recorded on a Perkin-Elmer Spectrophotometer Model 883 by using KBr disc technique. A portion of each finely ground sample weighing 1.5 mg was mixed thoroughly with 300 mg dry KBr powder (BDH, AR) in an agate mortar. The mixture was then transferred to an evacuable steel die, pumped down for 2 to 3 minutes to remove air and finally pressed at 6 tonnes to form a translucent pellet 12 mm in diameter. Polystyrene film was used to calibrate the spectral recording of the equipment before scanning the sample. The disc was then placed in the disc holder in the spectrophotometer and scanned from 4000 to 500 cm^{-1} .

Results and Discussion

The IR spectra of the four samples gave characteristic peaks of sulphate, water as well as phosphate ions. The absorption peaks present in the IR spectra of the four samples are computed in Table 1. More details of these peaks are discussed below.

Absorption bands of water molecules

The spectra show the absorption bands of water in 2 regions. The band in the 3500 cm^{-1} region (due to OH stretching) is resolved into two components. A number of workers have given different interpretations to this splitting^{8,9}. According to the most plausible explanation provided by Alder¹⁰ and Mitra¹¹, these two bands are due to two different modes of vibration which result from the presence of identical but specially non-equivalent OH groups which give rise to degeneracy. Strong coupling takes place between these groups, allowing the degeneracy to breakdown and result in the splitting of the band.

It is observed from Figs 1-3 that the OH stretching frequencies of A, B and C are shifted to higher values

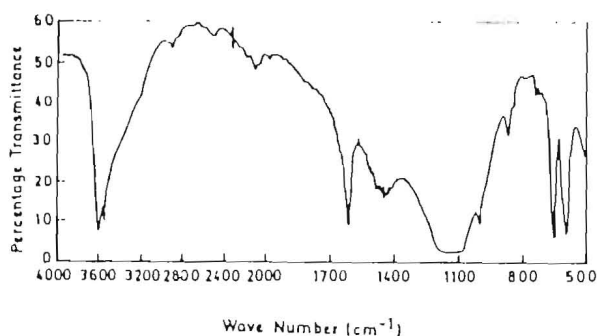


Fig. 1—IR spectrum of treated phosphogypsum sample A

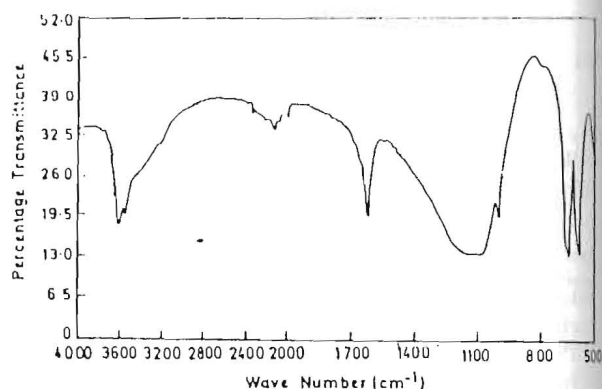


Fig. 2—IR spectrum of treated phosphogypsum sample B

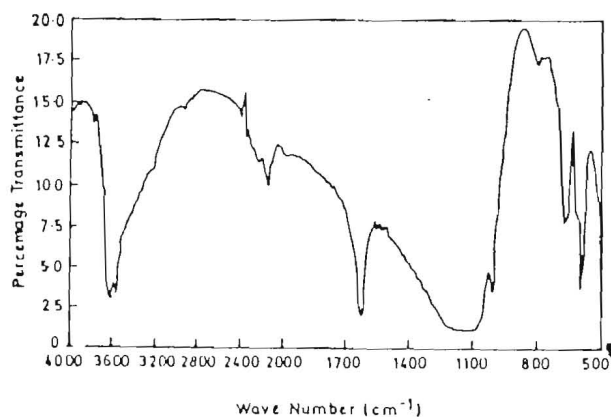


Fig. 3—IR spectrum of treated phosphogypsum sample C

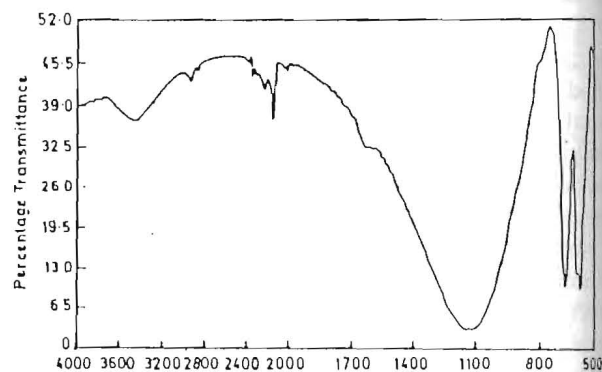


Fig. 4—IR spectrum of treated phosphogypsum sample D

than those of gypsum (3540 cm^{-1} and 3400 cm^{-1}) indicating that they could be hemihydrates. This is so because unlike gypsum, hemihydrate contains fewer water molecules with the result that few OH groups would have formed weaker hydrogen bonding which result in shifting of frequencies to higher values.

The other absorption band due to internal bending vibrations of OH (ν_2) is obtained at 1625 cm^{-1} in the three compounds (A to C). The absorption peak at 1680 cm^{-1} which is characteristic of gypsum is absent in all the compounds.

The IR spectrum of sample D (Fig. 4) does not show either the split peaks (3500 cm^{-1}) nor the 1620 cm^{-1} peak. These confirm that this sample could be an anhydrite. The presence of very weak and broad absorption band around 3500 cm^{-1} could be due to incomplete removal of water of crystallization.

Weak absorption peaks between 2400 cm^{-1} to 2000 cm^{-1} in all the cases (Table I) may be due to the presence of associated water as well as moisture absorption either in samples or in KBr⁷.

Absorption bands of sulphate ion

The most important IR absorption bands in gypsum and related compounds are due to SO_4^{2-}

bendings and stretching vibrations. The absorption due to bending mode (ν_4) is observed in the form of two distinct peaks. One a lower frequency peak at 600 cm^{-1} and the other a higher frequency peak at 670 cm^{-1} . The first peak was observed in all the four samples around 600 cm^{-1} .

The higher frequency peak was observed at 665 cm^{-1} in the case of A and B which is close to 660 cm^{-1} observed for hemihydrate. This peak was observed at 675 cm^{-1} in the case of D which is the characteristic frequency of absorption for anhydrite. However, shifting of this absorption peak in the case of C which is a hemihydrate needs to be explained. Very weak absorption peak is observed at 615 cm^{-1} in D which is usually present at 620 cm^{-1} in anhydrite. The presence of a number of components of vibrational mode (ν_4) indicate the degradation of high symmetry of SO_4^{2-} molecules in various forms of CaSO_4 . Alder and Kerr¹² have explained the multiplicity of absorption peaks in this mode due to the presence of non-equivalent SO_4 ions in the unit cell, the number of vibrational components exceeding the number permitted by the site symmetry.

The stretching vibrational mode (μ_3) of SO_4 ion is observed in the form of very strong and broad band in

Table 1. Infra-red spectral data of treated phosphogypsum samples (A-D)

Frequency mode	A	B	C	D	Possible assignment
$\nu_1 \text{SO}_4$	605 s	602 s	600 s	598 s	SO_4^{2-} bending vibrations
	665 s	665 s	680 m	615 vw	
	760 w			675 s	
$\nu_1 \text{SO}_4$	880 w	820 vw	805 vw	---	PO_4^{3-} stretching vibration
	1010 w	1010 w	1010 w	---	
$\nu_2 \text{SO}_4$	1090 vs	1090 vs	1090 vs	1100 vs	SO_4^{2-} stretching vibrations PO_4^{3-} adsorption bands may be mixed up
	1180 vs	1160 vs	1190 vs	1160 vs	
$\nu_1 \text{H}_2\text{O}$	1625 s	1625 s	1625 s		OH bending vibrations due to H_2O Absorption bands of associated water
	2140 w	2160 w	2140 w	2140 w	
	2210 vw	2210 vw	2230 w	2240 w	
$\nu_1 \text{H}_2\text{O}$	3565 m	3565 m	3560 m		OH stretching vibrations
$\nu_1 \text{H}_2\text{O}$	3620 s	3620 s	3615 s		due to H_2O

the range 1180-1090 cm^{-1} . Weak absorption band at 1010 cm^{-1} is observed due to stretching vibrational mode of SO_4^{2-} (ν_1) in case of A, B and C. This band is also characteristic of hemihydrate. As expected this band is absent in D.

Absorption bands of phosphate ion

Phosphates normally absorb strongly between 1100-1000 cm^{-1} . The presence of weak bands at 1010 cm^{-1} in case of A and B may be due to stretching vibration of PO_4^{3-} which may be mixed up with ν_1 mode of SO_4^{2-} stretch vibrations. Similarly absorption due to PO_4^{3-} in the region of 1100 cm^{-1} may be mixed up with very strong SO_4^{2-} stretching band (ν_1). Weak absorption peaks at 820 cm^{-1} and 805 cm^{-1} in the case of B and C respectively may be assigned to PO_4^{3-} stretching vibrations¹³.

The presence of very weak peaks due to PO_4^{3-} in all the cases may be due to the fact that all these byproduct gypsum samples were first thoroughly washed with water in order to remove the dissolved impurities, so as to use them for the manufacture of building materials.

Conclusion

Infra-red spectroscopy was used for quick identification of various forms of CaSO_4 -water system in phosphogypsum without resorting to time-consuming chemical/gravimetric methods. The results show that three of the four samples A, B

and C were hemihydrate phosphogypsum while sample D was an anhydrite.

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