

An infrared and Raman spectroscopic study of yellow gypsum synthesized from LD slag fines

Abstract

The present paper describes the characterization study of a yellow gypsum material synthesized from LD slag fines by using Fourier transform infrared (FT-IR) spectroscopy and Raman spectroscopy. The yellow gypsum was synthesized by the atmospheric leaching of -60 mesh LD slag fines obtained from the waste recycling plant (WRP) at Tata Steel plant, Jamshedpur, India, using sulphuric acid. The FTIR spectrum of the material was found to be exhibiting the characteristic absorption bands for gypsum. The study also revealed that the peak assignments in the Raman spectrum confirmed the presence of both gypsum and anhydrite phases in the material which could be correlated with the findings of the x-ray diffraction (XRD) analysis.

Keywords: yellow gypsum, ld slag, FTIR, Raman spectroscopy

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Introduction

LD slag is the by-product produced during the Linz-Donawitz or the LD process of steel making in an integrated steel plant at a rate of about 125 kg/t of the steel produced which leads to piling of the slag in the plant. This slag is generally recycled in a waste recycling plant (WRP) so as to separate the magnetic and the non-magnetic portions by means of mechanical crushing and magnetic separation. The magnetic portion is then recycled and used in the primary steel making process, whereas the non-magnetic portion is further processed at the WRP and stocked separately. This non-magnetic or reject portion of the slag currently has applications in the road construction sector where it is used as a replacement for aggregate.¹⁻⁴ Carbon dioxide sequestration using LD slag has also been an area of growing research.⁵ The slag is also useful as an excellent replacement of commercial lime used in fluxing of sinter. Thus, the piling of the reject slag is avoided and conservation of natural resources is also ensured.⁶ However, with this high rate of generation of LD slag (about 125kg per ton of steel), these applications are not sufficient and further value addition of the slag needs to be explored.

In this context, it is noteworthy that LD slag is highly basic in nature and is a rich source of calcium which is evident from the typical composition of LD slag. So, it will be worthwhile to explore the synthesis of industrially relevant calcium based materials from LD slag. Therefore, the objective of the present study is to synthesize and characterize a value added calcium product from the reject portion of the slag. This has been achieved by the synthesis of yellow gypsum by the atmospheric leaching of the slag using sulphuric acid. Gypsum is an important material having potential uses in different industries such as medicine, pottery, construction and the fertilizer sector. In this context, one question may arise as why the synthesis of gypsum from LD slag fines was attempted in this work. To address this question, it is important to know that presently gypsum is obtained after extensive mining. Therefore, one of the objectives of the authors, in this work, was to attempt the conservation of natural gypsum and at the same time produce a value added product from LD slag fines which is stock piled in the plant. In this manner, the disposal of LD slag fines can

be also effectively ensured by avoidance of using landfills for the same which can contribute to pollution of the environment. Sulphate minerals like gypsum have been studied by various methods like X-ray diffraction,⁷ Raman spectroscopy⁸ and infrared spectroscopy.⁹ The infrared and Raman spectra of gypsum and other sulphate bearing minerals like barite have been studied in detail by various authors.¹⁰⁻¹⁶ Till recently, spectral properties of gypsum, bassinette and anhydrite were studied to detect these mineral in mars by Bishop LJ et al.,¹⁷ in a report submitted to American mineralogist.¹⁷ Raman spectra of gypsum, bassinette and anhydrite were also studied by.¹¹⁻¹⁹ In the present paper, the authors have tried to correlate the findings of the earlier reported characterization techniques described during the synthesis of gypsum from slag in their earlier studies^{20,21} with the infrared and Raman spectra analysis in the present work.

Materials and methods

Synthesis of yellow gypsum

Synthesis of yellow gypsum was carried out as described in our previous work.²¹ Atmospheric leaching of -0.25mm LD Slag fines was carried out using sulphuric acid (specific gravity: 1.84, make: E-Merck, India). This process can be briefly described as follows. LD Slag fines, sulphuric acid and double distilled water were mixed in a ratio of 1:1.4:7.6 and heated at 105-110°C for twohours with constant stirring so as to obtain a slurry. The content of this slurry was basically insoluble calcium sulphate and other soluble salts. The slurry was then neutralized with 20% lime slurry in water (by using water and lime fines generated at the lime plant). The solid component was then separated from the filtrate and was dried at 50-60°C in a laboratory oven for 24hours. This dried product was designated as yellow gypsum and was then characterized using three techniques namely, XRD, FTIR and Raman spectroscopy. XRD technique which works on the principle of Braggs law and is useful in the measurement of crystalline sample. The XRD technique is also helpful in distinguishing the mixture and compound. FTIR is absorption based where the sample is exposed to a range of wavelengths of light and the amount of light absorbed by the sample is compared to a reference

and a difference spectrum is produced and Raman spectroscopy is a scattering measurement and in this technique sample is exposed to a single wavelength of light usually in the form of a laser and a range of wavelengths are monitored for light emitted. The light emitted is as a result of the interaction (Raman) of the material with that single wavelength light. It provides the information about the spectra of the molecule and chemical bonds. It is simple and provides the quick information. FTIR technique is sensitive to the dipole vibrations in O-H, C-H, and N-H bonds whereas Raman is sensitive to polarizable vibrations like those present in C=C, C=N, C≡N, and aromatics. The chemical composition of the material was also determined as described in ASTM C471M-01²² for the sulphur trioxide (SO₃) content and by ICP-AES technique for determination of the impurities as described in our earlier work.^{20,21}

Results and discussion

Correlation of XRD analysis with chemical composition of yellow gypsum

The XRD analysis of the material was carried out on a PAN analytical make XRD Spectrometer (Model XPERT-PRO) and the XRD pattern is presented as Figure 1. It was observed from the XRD pattern that the material exhibited characteristic peaks of gypsum and the

anhydrite phase. The presence of the anhydrite phase predominantly over the hemi hydrate phase can be associated with dehydration of the sample during grinding for XRD sample preparation as mentioned by Roy et al.²³ Peaks representing fayalite and ilmenite phases were also observed which could be correlated with the presence of silica and titanium in the gypsum sample as shown in Table 1, which represents the chemical composition of the material. From Table 1, it can be also said that the name of the material can be traced back to the yellow colour imparted by the presence of iron in the material.

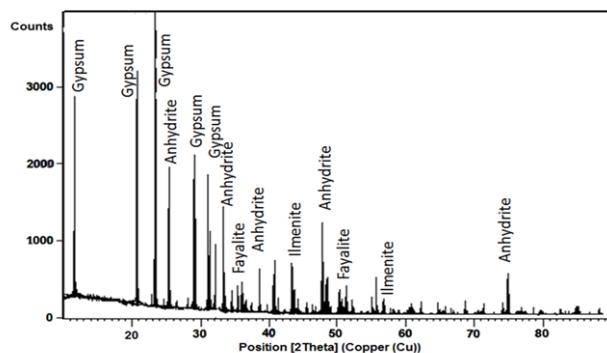


Figure 1 XRD pattern of yellow gypsum.

Table 1 Chemical composition of yellow gypsum

Parameters/Sample	Unit	FeO	CaSO ₄	SiO ₂	P2O ₅	MgO	MnO	Al ₂ O ₃	TiO ₂	Cr ₂ O ₃
Yellow gypsum	%	4.54	87.98	3.84	0.843	1.29	0.124	0.19	0.248	0.065

Findings of the FTIR spectra

A Nicolet 6700 series FTIR Spectrophotometer was used for recording the IR spectra of the synthetic gypsum. The instrument wave number ranges from 4000 to 400cm⁻¹ with an accuracy of 0.01cm⁻¹ and resolution of $\pm 4\text{cm}^{-1}$. The samples were pulverized using mortar and pestle and pellets were prepared by mixing with KBr and spectra were recorded. A pellet measures 1mm in thickness and 13mm in diameter. For each sample three pellet specimens were prepared and spectra were recorded in the region 4000 to 400cm⁻¹. The pellet specimen containing well resolved maximum number of peaks was taken for the analysis. Figure 2 represents the FTIR spectrum of the sample. Table 2 summarizes the wave numbers with the possible compounds and corresponding vibration for yellow gypsum. As described by Liu Y et al.,²⁴ the presence of the characteristic absorption bands at 3543 and 3409cm⁻¹ confirmed the identity of the material as gypsum. These peaks represent the symmetric stretch vibration modes of water. Similarly, the O-H bending vibrations were identified by the peak assignments at 1685 and 1621cm⁻¹ respectively. These two peaks indicate the presence of two crystallographic distinct types of water in the sample. One type of water is associated with the sulphate group through hydrogen bonding whereas the second type can be attributed to the direct linkage of water with the calcium ions. The peaks representing the stretching and bending modes of the sulphate group can be assigned at 669 m⁻¹ and 602cm⁻¹ as described by Boke et al.,²⁵ respectively. Other characteristic peaks for gypsum

were observed at 1128 and 2237cm⁻¹ respectively as described by Konecny et al.,²⁶ Vaculíková et al.²⁷

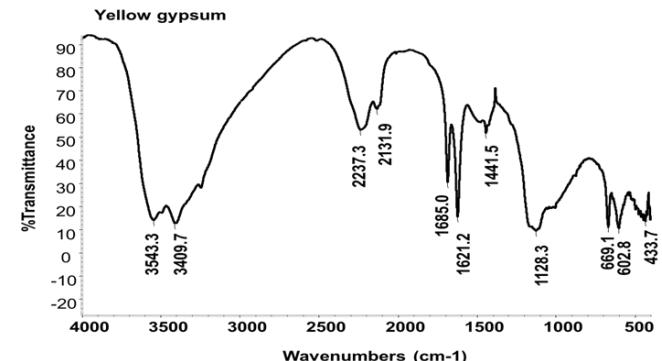


Figure 2 FTIR spectrum of yellow gypsum.

Raman Spectroscopy study

The Raman spectrum of the synthesized gypsum was performed by using a dispersive micro Raman Spectroscope (make: Thermo Electron Corporation Madison, U.S.A.). Adiode green (Nd YAG) laser beam of 532 nm wavelength was used to excite the samples. A very low power of laser beam (0.15mW) was employed to illuminate the surface. Prior to analysis of the samples, the instrument was

calibrated with pure silicon at the peak of 522 cm⁻¹. The spectrum is presented in Figure 3. From the Figure 3, it was observed that the peak assignments were similar to gypsum like materials as described by Liu Y et al.²⁴ The presence of a peak at 1008cm⁻¹ confirmed the characteristic v¹ symmetric stretch vibration mode for SO₄²⁻ tetrahedra in gypsum phase. The peaks at 497 and 408cm⁻¹ represented the symmetric bending v² vibration mode of SO₄²⁻ tetrahedra observed in the anhydrite phase. The v³ anti-symmetric vibration mode in gypsum was represented by a peak at 1135cm⁻¹. Similarly, peaks at 667 and

616cm⁻¹ were observed which represented the v⁴ anti-symmetric bending mode in gypsum respectively. The stretching vibration of water molecules in gypsum was also identified by the presence of two characteristic peaks around 3402 and 3492cm⁻¹ respectively. Thus, all the peak assignments indicate the presence of both the gypsum and the anhydrite phases in the sample and thus confirm the identity of the sample. These observations are in excellent correlation with the XRD analysis discussed as in section 6.1.

Table 2 Wave numbers of yellow gypsum

Sample type	Wave number	Literature (cm ⁻¹)	Corresponding vibration	Possible compounds
Yellow Gypsum	3543.3	3553	v ¹ symmetric stretch vibration modes of water	Bassinette ²⁴
	3409.7	3405, 3395	v ¹ symmetric stretch vibration modes of water	Gypsum ²⁴
	2237.3	2239, 2246	-	Gypsum ^{25,26}
	2131.9	2113	-	Gypsum ²⁴⁻²⁷
	1685	1685	O-H bending vibration modes	Gypsum ²⁴
	1621.2	1621	O-H bending vibration modes	Gypsum ²⁴
	1128.3	1130-1080		Gypsum ^{25,26}
	669.1	669, 680-610	Stretching mode of sulphate group	Gypsum ²⁷
	602.8	602, 612	Bending mode of sulphate group	Gypsum ²⁷
	433.7	400	-	OH bending bonds ²⁷

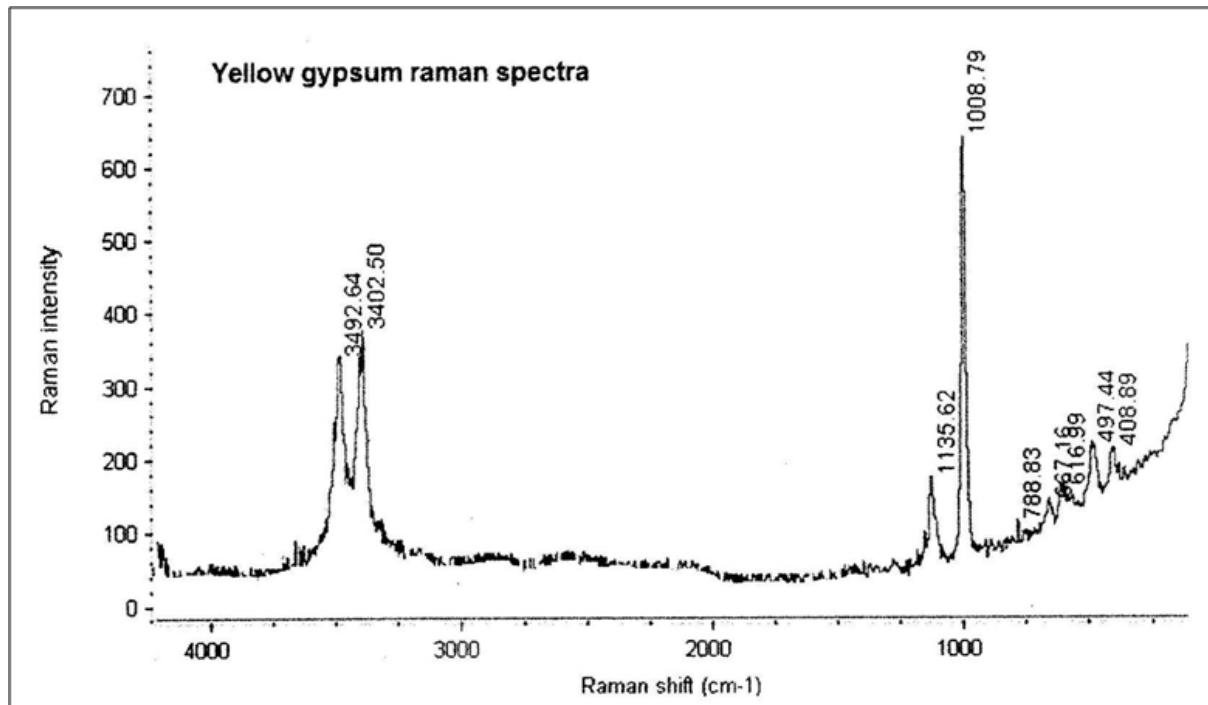


Figure 3 Raman spectra of yellow gypsum.

Conclusion

Synthesis of yellow gypsum material was successfully done by using LD slag fines obtained at the Tata Steel plant, Jamshedpur. The characterization of the material confirmed the formation of the material. The XRD analysis confirmed the presence of the gypsum and the anhydrite phases in the material which was also confirmed by the corresponding peak assignments in the Raman spectrum. The observations of the FTIR spectrum also confirmed the identity of the material as yellow gypsum. The presence of silica, iron and titanium in the material was confirmed by the chemical composition as well as with the findings of the XRD pattern. The study also resulted in filing of an Indian patent application bearing application number 572/KOL/2014. The study has also reinforced the need for future studies on the large scale synthesis of gypsum and its application and feasibility in the field of agriculture and building materials.

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Conflict of interest

Author declares that there is no conflict of interest.

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