International Journal of Minerals, Metallurgy and Materials
Volume 19, Number 4, Apr 2012, Page 279
DOI: 10.1007/s12613-012-0551-0

Chemical leaching of an Indian bituminous coal and characterization of the products by vibrational spectroscopic techniques

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(Received: 29 April 2011; revised: 28 November 2011; accepted: 29 November 2011)

Abstract: High volatile bituminous coal was demineralized by a chemical method. The vibrations of the “aromatics” structure of graphite, crystalline or non-crystalline, were observed in the spectra at the 1600 cm^{-1} region. The band at 1477 cm^{-1} is assigned as V_R band, the band at 1392 cm^{-1} as V_L band and the band at 1540 cm^{-1} as G_R band. Graphite structure remains after chemical leaching liberates oxygenated functional groups and mineral groups. The silicate bands between 1010 and 1100 cm^{-1} are active in the infrared (IR) spectrum but inactive in the Raman spectrum. Absorption arising from C–H stretching in alkenes occurs in the region of 3000 to 2840 cm^{-1}. Raman bands because of symmetric stretch of water molecules were also observed in the spectrum at 3250 cm^{-1} and 3450 cm^{-1}. Scanning electron microscopy analysis revealed the presence of a graphite layer on the surface. Leaching of the sample with hydrofluoric acid decreases the mineral phase and increases the carbon content. The ash content is reduced by 84.5wt% with leaching from its initial value by mainly removing aluminum and silicate containing minerals.

Keywords: bituminous coal; characterization; graphite; leaching; vibrational spectroscopy;

1. Introduction

Raman spectroscopy had been used extensively to characterize the structural features of carbonaceous matter since Tuinstra and Koenig [1] first correlated Raman bands to structural parameters measured from X-ray diffraction (XRD) of polycrystalline graphite. Raman spectroscopy had also been applied to study the structural features of coal-derived products [2-3]. In these studies, the Raman spectral characteristics, mainly those of graphite (G) and defect bands (D), were used to investigate the coal structures and their correlation to other characteristics, e.g. coal rank and the ‘graphite’ crystalline size parameters. In nearly all spectroscopic studies of organic and inorganic materials it is desirable to obtain Fourier transform (FT) Raman spectra along with Fourier transform infrared (FTIR) spectra. The two methods are completely complementary and could provide considerable structural information when used together.

The minerals present in coal play a significant role in the ash content of the coal. It will in turn affect the quality of coal as fuel. Concerted efforts are there to demineralize the coal samples to get mineral free coal [4-5]. In the present study, the change of functional groups and mineral group with hydrofluoric acid (HF) leaching on high volatile Indian coal was investigated by IR and Raman spectroscopy. Surface characteristics of very low ash bituminous coal obtained after chemical demineralization were carried out with scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

2. Experimental

The sample, in as-received condition, was powdered and dried in a dessicator to remove the absorbed water. Samples were leached with concentrated HF (30%-10%) for 24 h and washed with enormous amounts of distilled water. The slurry was filtered and dried at about 80°C for removing the absorbed water and allowed to cool slowly in a dessicator. The FTIR spectrum was recorded by a Shimadzu FTIR-8400

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spectrometer in the region of 4000-400 cm^{-1}. The Raman spectra were obtained using a Bruker RFS 100/S spectrometer equipped with a Raman accessory. This comprised a Spectron laser system SL301 Nd-YAG laser operating at a wavelength of 1064 nm, and a Raman sampling compartment incorporating 180° optics. The Raman detector was a highly sensitive standard Ge detector and was operated at 22°C. Under these conditions Raman shifts would be observed in the spectral range of 3500-1200 cm^{-1}. A laser power of 200 mW was used.

SEM micrographs of the virgin and residual samples were obtained by scanning electron micrograph (SEM) JEOL model JSM-6390 LV. Each of the samples was mounted on disc and coated with gold. The energy dispersive spectrometer (EDS) was obtained by JEOL model JED-2300. Elemental analysis was carried out using VarioEL III CHNS analyzer.

3. Results and discussion

3.1. Vibrational spectroscopic analysis of bituminous coal

The Raman spectra of the bituminous coal sample and the HF leached products within 1200-1650 cm^{-1} region are shown in Fig. 1. On studying the structures of the bituminous coal samples using Raman spectroscopy, the G band at 1598 cm^{-1} and the D band at 1345 cm^{-1} are commonly assigned as the graphite and defect bands respectively [4-7]. The bands in the region between G band and D band are assigned as V_R band (standing for valley right) at 1480 cm^{-1}, V_L band (standing for valley left) at 1388 cm^{-1} and G_R band (standing for G right) at 1542 cm^{-1}, prior to the literature information [6]. The band at 1477 cm^{-1} is assigned as V_R band, the band at 1392 cm^{-1} is assigned as V_L band and the band at 1540 cm^{-1} as G_R band. These bands represent mainly the aromatic semi-quadrant ring breathing for aromatic ring systems having more than two fused benzene rings.

The bands observed at 1460 and 1375 cm^{-1} in the Raman spectra of coal are attributed to CH band and absorption at ~1250 cm^{-1} is attributed to phenolic structures. The absorption due to phenoxy group at ~1250 cm^{-1}, presumably phenols, is probably very weak, and the major absorption is likely due to the graphite structure. This makes more sense to assign a small amount of this jointly to phenolic and CH structure and the major portion of the absorption to the graphite structure. Many of these bands with HF leaching decrease their intensities. In the Raman spectra of coal, weak absorption peak at 1080 cm^{-1} is observed. This is probably due to Si–O stretching or C–H band on aromatic rings [5]. This singlet with HF leaching was split up into three peaks with less intensity.

FT Raman spectra of bituminous coal and their chemical leached products with wavenumber 2600-3600 cm^{-1} are shown in Fig. 2. The vibrations of the CH_2 group, the asymmetric stretch, symmetric stretch and scissoring and wagging vibrations appear in the regions of 3000±50, 2965±30, 1455±55 and 1350±85 cm^{-1} respectively. Absorption arising from C–H stretching in alkenes occurs in the region of 3000-2840 cm^{-1}. For the two CH_2 groups, the asymmetric CH_2 stretching bands are observed at 2950 and 2920 cm^{-1} in the IR spectrum and only a weak band at 2940 cm^{-1} in the Raman spectrum. With HF leaching, the intensity of this band is decreased.

The C–H stretching in CH_3 group occurred at lower fre-

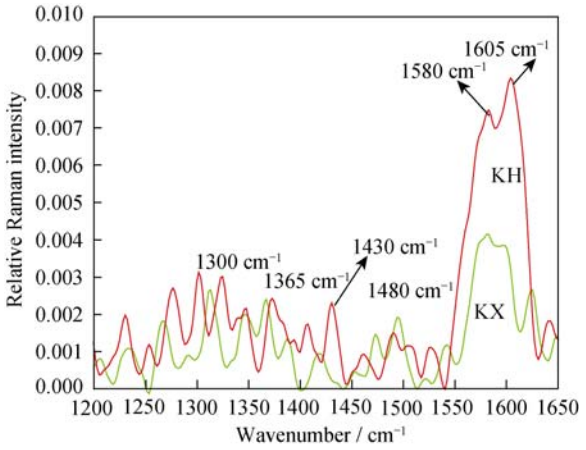

Fig. 1. FT Raman spectrum of bituminous coal (KX) and its HF leached products (KH) (1200-1650 cm^{-1} region).

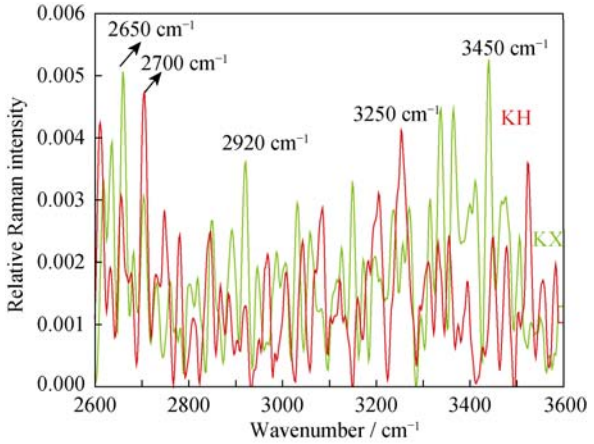

Fig. 2. FT Raman spectrum of bituminous coal (KX) and its leached product (KH) (2600-3600 cm^{-1} region).

quencies than that of the aromatic ring (3000-3100 cm^{-1}). In our present study, two weak bands appearing at 3020 and 3000 cm^{-1} in the FT-Raman are assigned to asymmetric stretching vibration. These bands are not visible in the IR spectrum.

The peaks in the 3000-3600 cm^{-1} region contain prominent peaks positioned at ~3250 and ~3450 cm^{-1}. The band at 3250 cm^{-1} in the spectra is attributed to the strong intermolecular coupling of water molecule symmetric stretch vibrations within a symmetric hydrogen bond. This band also arises because of OH stretching of Al–OH groups. The peak at ~3450 cm^{-1} in the spectra is assigned to the weaker coupling of the water molecule stretching modes, which is associated with a more disordered and asymmetric 4-coordinate (tetrahedral) hydrogen bonding network. This peak shows the decrease of intensity with HF leaching. The intensity loss could be correlated to the displacement of the water molecules in the symmetric hydrogen-bonding network by the halide (fluoride) ions. The fluoride ion, which is minimally polarizable, has no effect on the 3450 cm^{-1} peak in the Raman spectrum.

In the IR spectra of the coal sample (Fig. 3), in addition to the absorption band observed at 1605 cm^{-1}, absorption bands at 1435, 1375, 1165, 1105 cm^{-1} and a spike at 1030 cm^{-1} are observed. These bands indicate that the coal samples constitute complex polymeric materials, which were earlier reported by the same author in subbituminous coal [4-5]. The C–H bending frequencies have a higher intensity than the C–H stretching band. This is due to the intense broad absorption produced in this region by "graphite" components. Aromatics are also present in small amounts. With HF leaching, these bands remain more or less constant in bituminous coal. In Raman spectrum, bituminous coal shows more intense absorption with HF leaching in this region. The presence of graphite type, non-crystalline structure, is the most important contribution to the study of coal structure [6]. Graphite structure remains after chemical leaching liberates oxygenated functional groups and mineral groups. It is obvious that the graphite structure, crystalline or amorphous, would not be volatile or extractable. The present authors have the opinion that the changes in intensity of bands in the IR spectrum of coal are due to the liberation of extractable organic components of coal from the molecular sieve, which has been reported by many authors earlier [1].

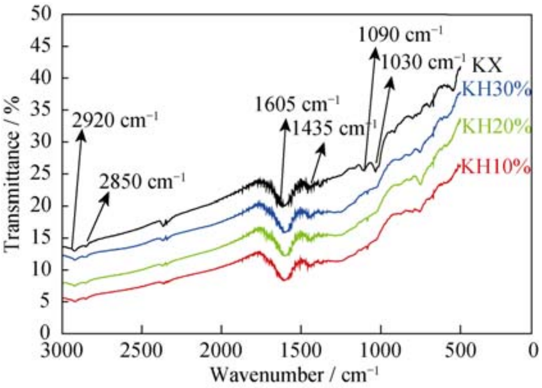

Fig. 3. FTIR spectrum of bituminous coal (KX) and its leached products (KH) (HF 10%-30%).

The intense bands at 602 and 570 cm^{-1} are doubly assigned to halloysite and aromatic ring breathing. The band is infrared active but weak. The characteristic IR bands in the 680-600 cm^{-1} region are attributed to the C–H bending modes. This band might be due to ring breathing vibration present in the coal.

Characteristic doublets for α-quartz are observed at 797 and 778 cm^{-1} in the IR spectrum [8]. These absorption bands in bituminous coal with chemical leaching are eliminated. The intense infrared bands at 1014, 1036, and 1108 cm^{-1} are due to the silicate bands in the sample [7-13]. These peaks decrease their intensities in bituminous coal when treated with HF. This result is in confirmation with that of the earlier study on bituminous coal carried out by Wu and Steel [9]. The C–C stretching bands (1161-758 cm^{-1}) are weak in IR and not simple characteristic frequencies in Raman. The identification of these vibrational bands is more difficult because other types of C–C stretching vibrations also occur in the same region (around 1300 cm^{-1}) and could interact with each other.

There are many weak Raman absorptions in the region 1200-1800 cm^{-1} other than graphite bands. The weak absorption band at 1540 cm^{-1} in the spectrum is assignable to the amorphous carbon structures with aromatics 3-5 rings. The bands at 1465 and 1380 cm^{-1} are due to methylene or methyl group, which indicate the presence of amorphous carbon structure in the sample. In the IR spectrum all these bands show a decrease in absorption with increase in HF concentration during leaching.

In addition to the above band, the in-plane deformation of CH_2 bands is observed at 1490 and 1460 cm^{-1} in the IR spectrum and at 1520 and 1460 cm^{-1} in the Raman spectrum of bituminous coal. The rocking modes of CH_2 are expected in the range of 895±85 cm^{-1}. This band is not prominent in the Raman spectrum of bituminous coal.

3.2. Minerals in bituminous coal

The SEM-EDS results of the coal sample are shown in

Fig. 4. It is seen that the samples are not very uniform, some points are rich in carbon, and at some points the minerals co-exist with the carbon materials. The EDS analysis of the surface reveals that, except for carbon, hydrogen, oxygen, nitrogen and traces of sulphur, silicon and aluminium (0.9wt% Al, 1.2wt% Si) are the major elements on the studied surface of Korba coal (Fig. 4). A bulk structure can be seen, which in turn is composed of a homogeneously distributed network comprised of small fistulous and filamentous crystallites showing minerals. Luminous and non-luminous features can be seen in the matrix. This indicates that the mineral grains are distributed in the organic matrix. Cracks and veins are also seen. The bright luminosity is due to the presence of lithophiles like aluminium and silicates. Chalcophile elements like sulphur are present only as trace elements.

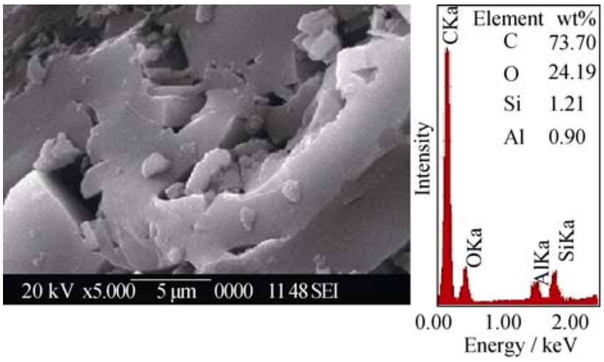

Fig. 4. SEM/EDS analysis of the virgin sample (KX).

3.3. Effect of HF leaching on demineralization

SEM-EDS analysis of the demineralized coal (Fig. 5) treated with 30% HF solution reveals that large particles of kaolinite and bassanite are extensively removed, and brightness of the surface is decreased. It can be seen that leaching caused morphological changes in the particle and did enormous modification to the surface by leaching of the inorganic minerals. Rubiera *et al.* reported a change in surface morphology in the case of bituminous coal when leached with 25% HF and nitric acid [10]. Estimation of the elemental composition by EDS shows that the surface has 81wt% carbon and 18.85wt% oxygen where as minerals like Si and Al are absent on the studied surface. The morphology of the coal shows a layer-like structure, which is characteristic of a graphite layer [9-13]. This further suggests that the mineral particles are not trapped in the coal layer, which may be easily separated using chemical leaching. The mechanism of fluoride attack is the reaction of hydrogen fluoride (HF) with silicon dioxide (SiO_2) to form silicon tetrafluoride (SiF_4):

$$4HF+SiO_2 \rightarrow SiF_4+2H_2O.$$

Silicon tetrafluoride is soluble in water and will react with additional hydrogen fluoride to form fluorosilicic acid (hexafluorosilicic acid) as follows:

$$2HF+SiF_4 \rightarrow H_2SiF_6 \quad \text{or} \quad SiO_2+6HF \rightarrow H_2SiF_6+2H_2O$$

This is removed during the leaching.

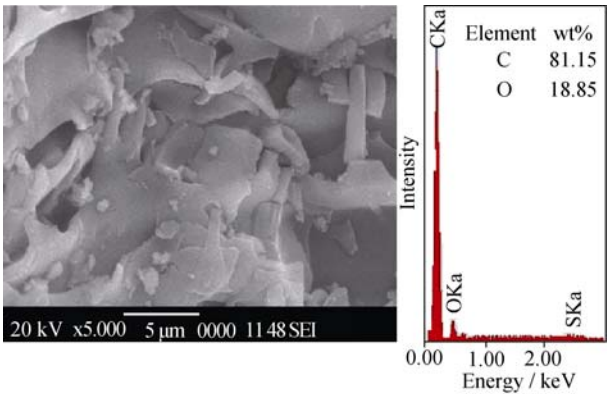

Fig. 5. SEM/EDS analysis of the HF leached sample (KH).

Table 1 shows the contents of C, H, N, S and O in the virgin coal (KX) and demineralized coal (KH). When bituminous coal is treated with HF (30%), the sulphur content decreased from 0.331wt% to 0.148wt% because of the reaction with bassanite. Other elements such as C, H and N increased during leaching whereas O content decreased from 22.54wt% to 15.207wt%. From the proximate analysis, it is found that the ash content decreased from 8.2wt% to 1.27wt% with HF (30%) leaching. Wu and Steel [9] earlier reported a reduction of ash content from 5.30wt% to 1.37wt% in UK bituminous coal by one-stage HF leaching. The present result is a better result than the previous reported ones. Leaching is performed with various concentrations of HF. As the concentration of HF in leaching increases, the ash content decreases by 84.5% (Fig. 6.).

Table. 1 Proximate & elemental analysis of virgin and HF treated sample

Coal	Proximate analysis / wt%				Elemental analysis by ultimate analysis wt%				
	Fixed carbon	Volatile matter	Ash	Moisture	C	H	N	S	O
KX	55.39	28.98	8.20	5.40	69.90	5.71	1.50	0.33	22.59
KH	65.05	28.58	1.27	5.10	74.59	8.39	1.67	0.15	15.20

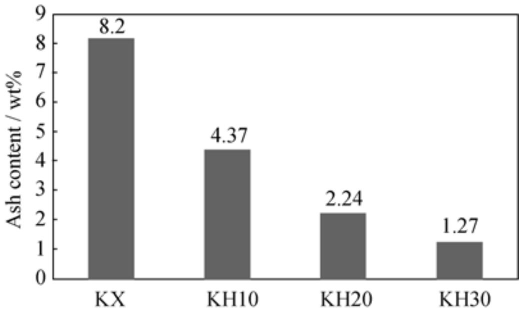

Fig. 6. Effect of HF leaching on demineralization.

4. Conclusions

The vibrations of the "aromatics" structure of graphite, crystalline or non-crystalline, were responsible for the observed spectra in the 1600 cm^{-1} region. The band at 1477 cm^{-1} is assigned as V_R band, the band at 1392 cm^{-1} as V_L band and the band at 1540 cm^{-1} as G_R band. Graphite structure remains after chemical leaching liberates oxygenated functional groups and mineral groups in the sample. In the IR spectrum all these bands show a decrease in absorption with an increase in HF concentration with leaching. Characteristic doublet for α-quartz at 797 and 778 cm^{-1} in the IR spectrum and this band is removed with leaching. The intense infrared bands at 1014 cm^{-1}, 1036 cm^{-1} and 1108 cm^{-1} are due to the silicate bands in the sample. These peaks decreased the intensity in bituminous coal when treated with HF. The peak at ~ 3450 cm^{-1} in the spectra is assigned to the weaker coupling of the water molecule stretching modes. This band showed a decrease in intensity with HF leaching. The intensity loss could be correlated to the displacement of water molecules in the symmetric hydrogen-bonding network by halide (fluoride) ions. The morphology of the coal shows a layer-like structure, which is characteristic of a graphite layer. Leaching using HF decreases remarkably the ash content in high volatile bituminous coal from 10.23wt% to 1.27wt%. From the ultimate analysis it is found that the carbon content is increased from 69.90wt% to 74.59wt% with leaching whereas oxygen content decreased from 22.59wt% to 15.207wt%.

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