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EXTRACTION OF CARBONYL, CARBOXYL FUNCTIONAL GROUPS AND SILICATE MINERALS FROM COAL AND ITS CHARACTERIZATION USING INFRARED SPECTROSCOPY

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ABSTRACT

This paper reports the characterization and demineralization of coal with HCL, Chloroform and water. The residual coal from each treatment was analyzed using FTIR spectroscopy to understand the effect of chemical leaching and water washing on the sample structure for aliphatic and aromatic CH bonds. Investigation of the mineral content in the sample and its change with above said treatment was also done. Absoptivities for aromatic CH bond stretching and out-of-plane bending modes were found to be independent of the structure. For structural analysis of coal, the structural independence of absoptivities for aromatic CH bonds allows a reliable assessment of aromatic hydrogen content in coals. Evaluation of aliphatic hydrogen content was greatly affected with the presence of chloroform extractable in the coal, which contain highly aliphatic material with a high absoptivities of aliphatic CH bonds, especially those in long methylene chains. The absoptivities of

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heteroatom-rich fractions were lower than those of hydrocarbons and did not show any dependence on hydrogen aromaticity of the sample.

Key words: Coal, Chemical leaching, FTIR

1. Introduction

Due to its origin, coal is a chemically and physically extremely complex and heterogeneous material, consisting of organic and inorganic constituent. The acceptance of a coal for a particular process in industry depends critically on both components. The organic structure of coal can be regarded as consisting of heterogeneous aromatic structure, with aromaticity increasing from low rank (lignite) to high rank coals (anthracite). The organic part of coal also contains sulphur, oxygen, and nitrogen in functional groups. Fourier transform infrared (FTIR) spectroscopy is a widely used analytical technique for determining the different functional groups in coal structure. This method, being able to reveal carbohydrogenated structure (aromatic and aliphatic) and hetro atomic functions (mainly oxygenated) as well as to detect the presence of minerals, is currently one of the most powerful techniques for coal characterization and thus is of paramount importance in the various utilization procedure of coal. The use of low rank coals in industrial combustion may affect the performance of furnace by forming slag in the bottom of furnace, which in turn affect efficiency and may leads to costly repairs. The effluent gas coming out of furnace may increase pollution. Characterization and various demineralization techniques have been done by various groups [1-6]

In the present study, FTIR spectra of sub bituminous coal sample collected from Korba coal field, south central India, were collected in order to investigate the chemical structure of these semi ranked coals, as well as their change in mineral content when treated with concentrated hydrochloric acid (HCl) and chloroform. The same sample is subjected to washing with water and the change in structure of the minerals is studied. The present study is restricted to the absorption bands within the range 2000cm^{-1} to 400cm^{-1} mainly because almost all minerals and carboxylic groups show absorption in this region.

2. Experimental

2.1. Extraction procedure

Samples are collected by random picking from a borehole situated in Korba fields. The sampling depth is around 150m from ground level. The sample is crushed into coarse fragments, air dried at room temperature for about 100 days, and then ground to a grain size of about 5μm. Specimens for FTIR are prepared using the potassium bromide(KBr) pellet technique. A very small amount of sample (about 1mg) is mixed with 200mg of KBr to produce the pellets. The analysis is carried out on a Shimadzu-8400 FTIR Spectrometer at a resolution of 4cm^{-1} in the spectral range 400-2000cm^{-1}. Bands are identified by comparison to published assignments [1-12]. The samples are treated with concentrated HCl and chloroform for 72hrs inpendently and after removing the extractable dried in a temperature of about 100°C. Another set of sample is washed with water. FTIR spectrum of the chemical leached samples and water washed samples are recorded as discussed above. The effect of chemical leaching and washing on the prominent bands are studied

3. Results and Discussion

3.1 Characterization of the row coal sample

The FTIR spectrum of row sample is shown in figure 1. Most prominent bands are identified and shown in the table 1. The spectrum is dominated by the absorption bands of inorganic material present in the sample. Absorption band due to the carbonates near 1450-1410 cm^{-1}, 880-860 cm^{-1} and 720-680cm^{-1} are not clearly resolved because of the low concentration of carbonates.[4]. Strong sharp band at 1695cm^{-1} and strong prominent band at 1605cm^{-1} observed in all the samples can be attributed to carboxyl and C=C stretching respectively. Starsinic et al. [13] assigned the band at 1695cm^{-1} to carboxyl groups, possibly Ketones. Supaluknari et al. [16] observed the bands at 1695cm^{-1} and 1605cm^{-1} in the case of brown coals and oxygen rich bituminous coals, while in higher rank coals with low oxygen content the absorption at 1695cm^{-1} appears as shoulder on the 1605cm^{-1} band [13-15]. The strong band near 1695cm^{-1} is attributed predominantly to carboxylic acid and a relatively weak band at 1670cm^{-1} is assigned to ketonic structures. They also observed that the total absorbance of all the carboxyl bands for the brown coal is greater than those for the higher rank coal samples. The brown coal with higher oxygen content contain less amount of carboxyl group and has a lower intensity for 1695cm^{-1} band than brown coal with low oxygen content.

It is clear that the samples having higher oxygen content have low intensity absorption band at 1695cm^{-1} while the samples having low oxygen content show well resolved and intense band at 1695cm^{-1}. The presence of sharp absorption band in the spectra shows that the coal samples contain less oxygen content. Such a result is in conformity with the observations of Supaluknari et al. [16] in the case of oxygen rich Australian Brown coal. A very pronounced absorption band at 1605 cm^{-1} is present in all the coal samples, due to C=C aromatic stretching. Motterra and Low [15] found the band at 1605 cm^{-1} in the case of wood charcoal and assigned it to aromatic C=C vibrations. Low and Glass [17] made elaborate discussion of 1605 cm^{-1} band of coal. They assigned the band in case of in low rank coals and chars which have been formed at relatively low temperature, to aromatic ring stretch of small, discrete aromatic entities. They also suggested that the oxygen containing structure may or may not be involved in the formation of 1605 cm^{-1} band.

On the basis of above observations the band observed at 1605 cm^{-1} can be attributed to aromatic ring stretch of small, discrete aromatic groups present in the sample. Absorption bands of silicate minerals near 1100-800 $cm^{-1}$and 600-400cm^{-1} are identifiable in the spectrum of raw coal. In addition to the above absorption band observed at 1605 cm^{-1}, broad bands at 1165, 1105 cm^{-1} and shoulder band at 1030 cm^{-1} has been observed in all the samples. Unresolved plateau like bands observed in this region shows that the coal samples constitute complex polymeric materials.

Olson et al. [18] found the band at 1030 cm^{-1} in the Beulah lignite sample and this band was assigned to the clay absorption. From the above observations the strong broad bands observed at1105cm^{-1} and 1030 cm^{-1} can be attributed to trace amount of silicate minerals associated with the sample.

Sobkowiak et al. [19] reported that sub bituminous coal samples have large absoptivities for different aliphatic –CH bonds, the highest being most likely for –CH bonds in long chain methylene structure. They also reported that the absoptivities for aromatic –CH bonds is very small. From the spectrum it is clear that at 720cm^{-1}, the sample shows a moderate absorption which is due to presence of long chain methylene structure. Medium absorption bands in the region 915cm^{-1} and 756cm^{-1} is due to aromatic –CH out of plane structure [18]. From this information we can conclude that the sample is high ranked high volatile bituminous coal.

The region between 900-690cm^{-1} is due to the out of plane C-H bending due to aromatic rings. These are extremely intense absorptions, resulting from strong coupling with adjacent hydrogen atoms and can be used to assign the positions of substituents on the aromatic ring. Aromatic ring stretch absorptions occur in pairs at 1600cm^{-1} and 1475cm^{-1}.

The strong absorption near 690$cm^{-1}$is due to the presence of mono substituted ring. Second strong band usually appears near 750cm^{-1}. When the spectrum is taken in a halocarbon solvent, the 690cm^{-1} band may be obscured by the strong C-X stretch absorptions. It is clear from the figures 3 and 4 that the when the sample is treated with chloroform and HCl this particular band is shifted to higher wave numbers. The strong band near 750cm^{-1} is due to ortho-disubstituted rings (1,2-Disubstituted Rings) The absorption at 690cm^{-1} along with a band near 780cm^{-1} is because of the substitution pattern due to meta-disubstituted rings(1,3-Disubstituted Rings) The bands appearing in the 720cm^{-1} to 667cm^{-1} region is due to C=C out of plane ring bending vibrations.

3.2 Chemical leaching of the sample

The FT-IR spectra of the raw and the HCl and Chloroform washed samples were presented in fig 3 and fig4.The bands due to silicate remain more or less the same after the treatment with HCl. The same result was reported by Õztas et al in Turkish Zonguldak bituminous coal[4]. The following changes are observed in the spectrum. The band at 466cm^{-1}which is assigned to clay and ash slightly reduces its intensity when treated both with HCl and Chloroform [1,4]. The band at 540cm^{-1} and 669cm^{-1}is not showing any modification when treated with HCl but slightly reduces its intensity with chloroform. The band at 669cm^{-1} is shifted to lower wave length when it is treated with Chloroform [2] The SiO band at 696cm^{-1}decreases its intensity when treated with HCl and chloroform but surprisingly the SiO band at 750cm^{-1} is not modified with chemical leaching [2]. This confirms this band due to aromatic hydrogen as aromatic ring [1].The intensity of aromatic –OH out of plane bending bond at 798cm^{-1} slightly decreases with chemical leaching due to the removal of oxygenated group [1-2]. The CO group at 1031cm^{-1} is modified when treated with chloroform. This may be due to the presence of aliphatic group which can be extracted with chloroform than due to minerals [1]. The band at 1010cm^{-1} which corresponds to mineral matter shifted to lower wavelength when treated with HCl as shown in fig 3.The band near 1100cm^{-1} is also shifted to lower wavelength in the spectrum of HCl extract [3-4]. The aromatic stretching bond at 1602cm^{-1}is not changed with chemical leaching because aromatic stretching modes are not extractable with HCl or chloroform. The oxygenated functional groups (1800-1000cm^{-1}) show lower intensities in the non extractable material compared to raw sample, thus revealing the effectiveness of the extraction with chloroform or similar solvent. The band at 914cm^{-1} which corresponds to –CH out of plane bending reduces its intensity when extracted with chloroform [1-2]. The intensity of the mineral bands (400-600cm^{-1}) is preferentially increased in the FTIR spectra of the insoluble material. The band corresponding to long chain methylene disappeared when treated with chloroform. It is known that long-chain methylene most probably has the highest absorptivities among aliphatic hydrogen types. This hydrogen is most abundant in highly aliphatic waxes and resins that can easily be extracted with chloroform or a similar solvent. The variations in the absorptivities for aromatic CH bonds have been found to be much smaller (900-700cm^{-1}), among which the band near 821cm^{-1} and the two peaks near 791 and 784 cm^{-1} were found to be originating from aliphatic -CH bonds. The amount of chloroform extractable in coal can greatly affect the determination of aliphatic hydrogen content. Fig 5 shows a comparison of effect of various leaching on the same sample. It is found that, of the various methods, chloroform is the best leachant especially for -CH bonds and oxygenated functional groups.

3.3 Treating with water

The FTIR spectrum of the sample treated with water is shown in fig. 2. The band at 466cm^{-1} and 540cm^{-1} are slightly reduced in intensity mainly due to the removal of clay and silicate from the sample. The band at 653 cm^{-1} and 750cm^{-1} are not modified when treated with water. The band at 798cm^{-1} which is assigned for aromatic –OH out of plane bending is slightly reduced. The band between 1000cm^{-1}-1600 cm^{-1} is slightly decreased intensity with water treatment.

Conclusion

It can be concluded from the results that chloroform is a better leachant compared to hydrochloric acid and water to remove phenolic and alcoholic C–O bonds as well as C–O–C bonds. Chloroform leaching affect the determination of aliphatic hydrogen content in coal. There is no change in the aromatic hydrogen content with chloroform extraction. It is found from the study that they are coal with less oxygen and silicate content. It is also found that the structural dependence of -CH bond absoptivities depend on the amount of chloroform extractables in the coal.

Chemical leaching could moderately reduce clay minerals and ash, SiO of SiO_4 and aromatic –OH out of plane bending.

Water when used as a leachant could remove clay minerals and ash content but not much of silicates from the coal sample.

Table 1-Wave number Vs Probable assignment

Wave numbercm^{-1}	Assignment
466	Quartz and clay minerals
540	Silicate minerals
669	Aromatic out of plane CH deformation
690	Si-O of SiO_4/ Mono substituted ring
720	Long chain methylene

750	Aromatic hydrogen as aromatic ring
798	Quartz/CH bending vibration
914	-CH out of plane bending
943	OH out of plane bending
1010	Si-O stretching
1030	Phenolic or alcoholic C-O bonds/silicate group
1100	Quartz
1602	Aromatic C=C
1741	Carboxyl/carbonyl band

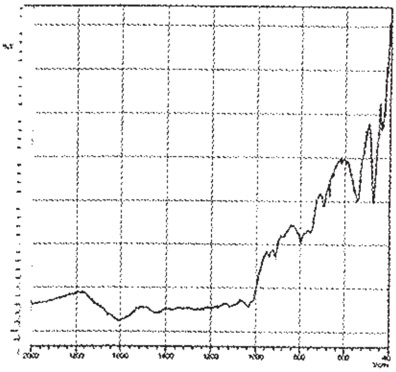

Fig.1. spectrum of Crude coal

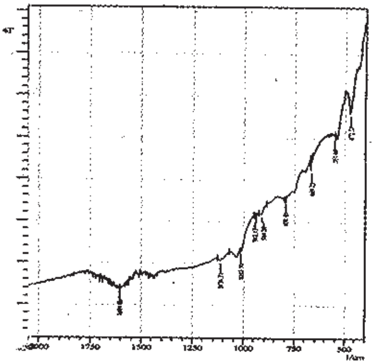

Fig.2. H_2O leached coal

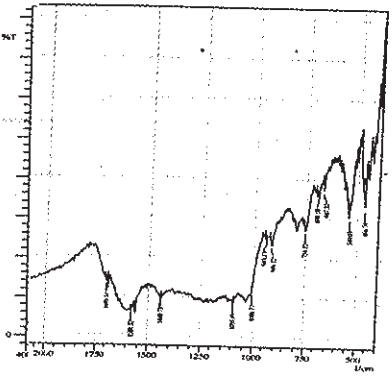

Fig.3. FTIR Spectrum of HCl Leached sample

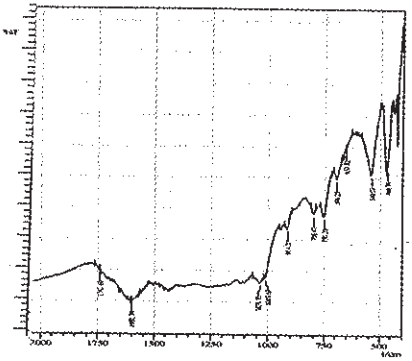

Fig.4. FTIR Spectrum of $CHCl_3$ Leached sample

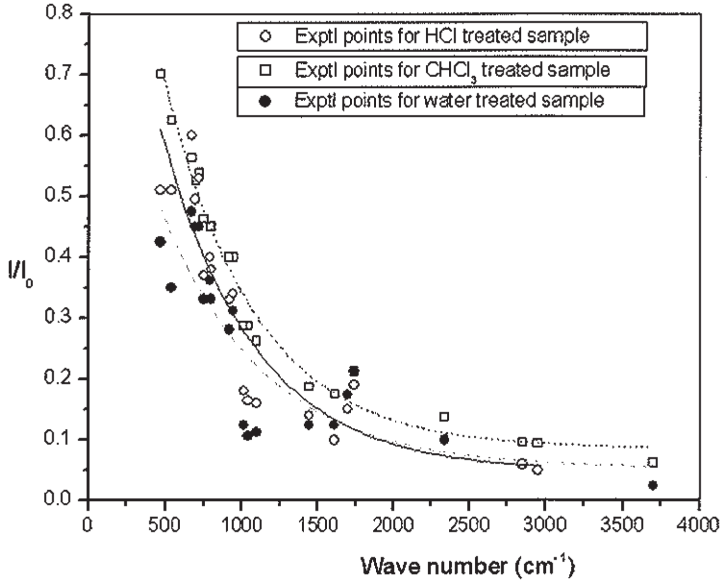

Fig.5. Ratio of transmission Vs wave number

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