

Study of Chemical State of Iron in Giral Lignite Samples using ^{57}Fe Mossbauer Spectroscopy

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^{57}Fe Mossbauer spectroscopy and powder XRD has been used to characterize the iron-bearing phase in the lignite samples collected from Giral, Rajasthan. It is found that the samples contain anomalous presence of Jarosite which is generally not found in lignite samples. Simultaneously powder XRD spectra show dominating presence of Ca_2SO_4 . It appears that both sulphate minerals (Jarosite and Gypsum Ca_2SO_4) should be highly correlated. The significance of anomalous presence of Jarosite in lignite samples is discussed.

Keywords: Mossbauer Spectroscopy, Giral Lignite, Jarosite and Gypsum.

1. INTRODUCTION

Coal is one of the major sources of fossil fuels present in nature. This is also used for the generation of electricity in power plants. Coal is consequently a sedimentary rock consisting of an organic part with added minerals diagenetic or syngenetic in origin. The composition and properties of coal are controlled by the original material, the condition of accumulation and method by which the material was converted into coal.

Coal is heterogeneous. It consists primarily of organic materials admixed with mineral matter including sulphur. The organic material in the coal that is derived through the process of coalification is essentially composed of large polymeric molecules in which chemical structures are variable and non-repetitive. However, the properties of coal appear to depend mainly on the physical and chemical structure of these organic compounds. The mineral matter may occur both as mineral species and as mineral phases of widely-varying particle sizes and also as species that are chemically complexed by the organic matter. It is believed that the physical structure of coal is represented by spatial arrangement of large complex molecules, along with a few much smaller ones. The same appears to be the case with products obtained from physical processing of coal. The physical as well as chemical properties of coal depend upon its physical structure, and the physical structure of coal may be studied without going into details of its chemical structure.

Coal is used in four main processes: combustion, coking, hydrogenation and pyrolysis. Over a length of time, coal has been used to produce power. However, great efforts are being made to obtain chemical products and liquid fluids. The mineral and elements present in coal play an important role in coal utilization. Previous work has reported that minerals in coal can give both problems and benefits in conversion processes [1,2,3].

The importance of mineral matter is in coal beneficiation. By coal beneficiation we mean any process used to improve the quality of coal, or make it easier to manage, transport and to store. However, in a more exact sense, coal beneficiation means to clean coal in order to obtain coal fractions concentrated in organic matter and reduced in mineral matter and inorganic elements.

It should be noted that in a coal more than about fifty different minerals can be found, although only a few appear in a significant proportion. Apart from organic component coal also contain inorganic minerals. The inorganic minerals in coal can be divided into two parts (i) Iron bearing minerals and (ii) non-Iron bearing minerals. Study of inorganic minerals is very much important for coal utilization.

The Iron bearing minerals which are major constituents of the coal mineral matter, can be identified using Mössbauer spectroscopy [4,5,6]. Despite the fact that Mössbauer Spectroscopy is restrained to analyze iron bearing minerals, it also gives information about presence of pyrite (FeS_2), which is one of the main producer of sulphur oxides in combustion processes. The presence of large pyrite concentration in combustion of coal can result in serious environmental problems due to the release of sulphur oxides. Moreover, pyrite is attacked by atmospheric oxygen, its oxidation may enhance those coal properties desirable for liquefaction procedures.

The Fourier Transform Infrared Spectroscopy (FTIR) is also frequently used to gather information about the organic part present in the coal [7,8]. There are several lignite coal fields in western Rajasthan like Palana lignite coal bed, Merta Road coal bed, Barsingsar Bikaner etc. Out of which Mössbauer spectroscopic analysis of Merta Road lignite is reported by Tripathi *et al.* [9]. Recently, we have reported Mössbauer spectroscopic study of Palana lignite formation [10]. So, It is worthwhile to extend study on other lignite coal bed also. In this context we have reported the study of major coal field, Giril lignite coal bed located in Barmer, Rajasthan, India.

In present study samples collected has been studied to characterize the inorganic mineral phases present.

The samples have been collected fresh from seven different seams LS-1, LS-2, LS-3, LS-4, LS-5, LS-6, LS-7 of Giril coal mines as shown in Figure 1 and also samples from in between depths of two consecutive seams GL-1, GL-2, GL-3, GL-4, GL-5, GL-8, GL-15, GL-16, GL-17, GL-18, GL-19, GL-20, GL-21, GL-22, GL-23, GL-24, GL-25, GL-28. Samples BK-1, BK-2, BK-3 collected from different seams of Barsingsar coal mines are studied.

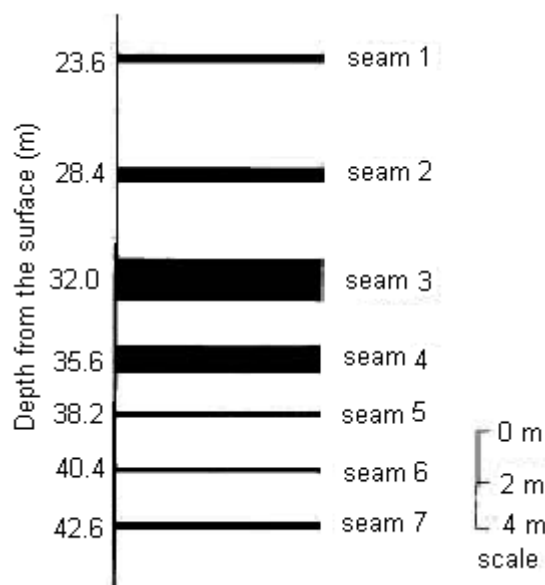


Fig. 1: Depths of different samples of seams in Giral coal mines.

2. EXPERIMENTAL

The lignite samples collected from different seams were crushed to obtain fine powders. Mössbauer absorbers were prepared by pressing the powder in a paper disk of diameter 25mm. A constant acceleration Mössbauer spectrometer was used with ^{57}Co source in the rhodium matrix. Calibration spectra with natural iron foil were taken before and after each experiment. The zero velocity channel was determined by locating the point of mirror symmetry (folding point) in each spectrum using a Fortran program. The Mössbauer data were analyzed using a Fortran program, after suitable modification, in which we assume spectral lines to have Lorentzian shapes. The two peaks of a quadrupole doublet were constrained to have equal width and equal amplitudes. The value of x_2 was mostly close to 1-1.1 per degree of freedom. The Mossbauer parameters reported here have accuracy up to ± 0.03 mm/s. It may be pointed out that in many of our spectra absorption peaks from different components overlapped. Therefore, the same spectrum could be fitted in more than one ways. In such cases, our decision has been based on the overall consistency across all the samples studied and the underlying pattern.

3. RESULT AND DISCUSSION

In Figure 2 and Figure 3 Mössbauer Spectra of representative samples are depicted and exhibit presence of two doublets. These are representative figures but all the samples show similar trend.

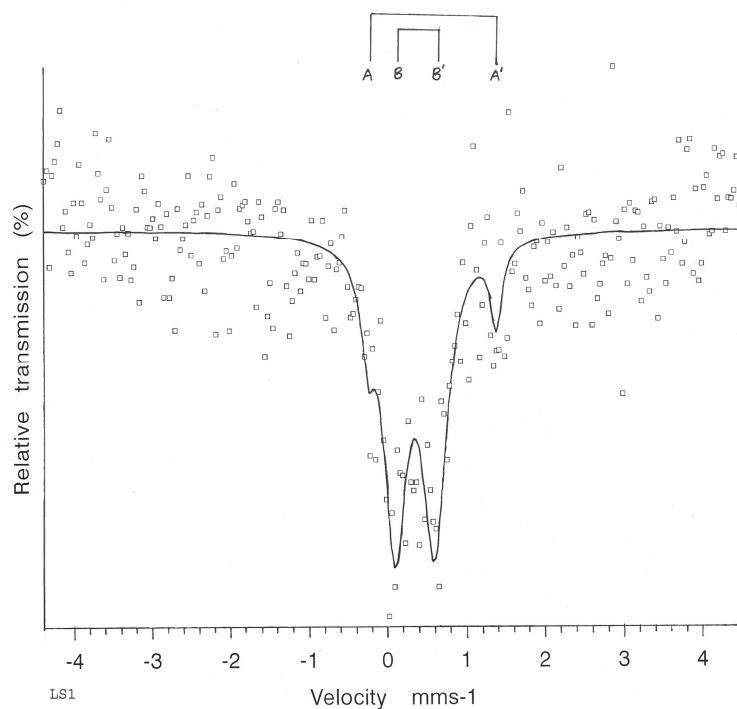


Fig. 2: Mossbauer spectra of lignite sample of LS-1.

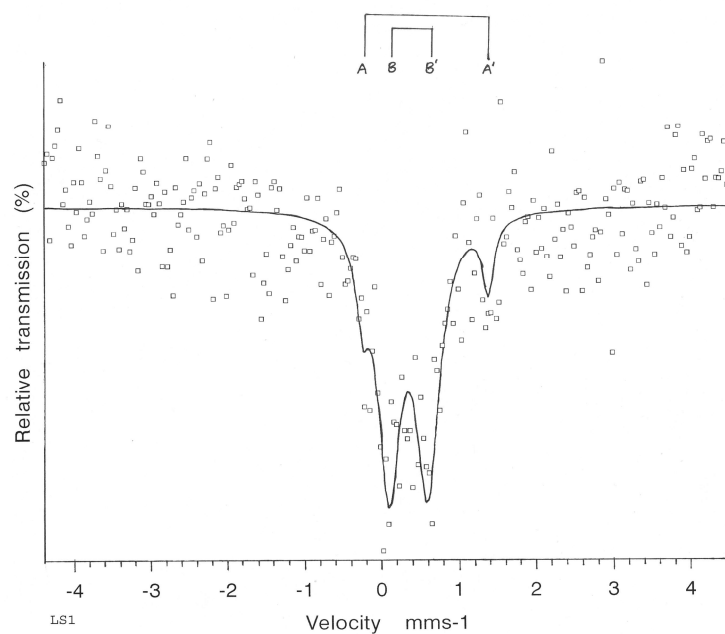


Fig. 3: Mossbauer spectra of lignite sample of LS-2

The assignment of doublets through the Mössbauer parameters appears in Table 1.

Table 1: Mössbauer parameters.

S. No.	Sample	Peak	Is (mms^{-1})	Qs (mms^{-1})	Lw (mms^{-1})	RA (%)
1.	LS1	A	0.5674	1.6345	0.178	1.1618
		B	0.3446	0.56505	0.369	88.3424

These two doublets BB' and AA' are resolved and show the most remarkable features of Jarosite & pyrite. An interesting feature of there lignite is the anomalous presence of Jarosite, an iron sulphate mineral which was not expected in coal. Such anomalous presence of Jarosite, is generally not found in coal sample though it may be present in meager amount due to oxidation of pyrite. It should also be noted that no other iron phase which may result due to oxidation of pyrite is absent like Goethite iron oxide etc..

Further, we also display powder X-ray diffraction pattern of the same sample shown in Figure 3, which shows dominantly presence of hydrated CaSO_4 (gypsum).

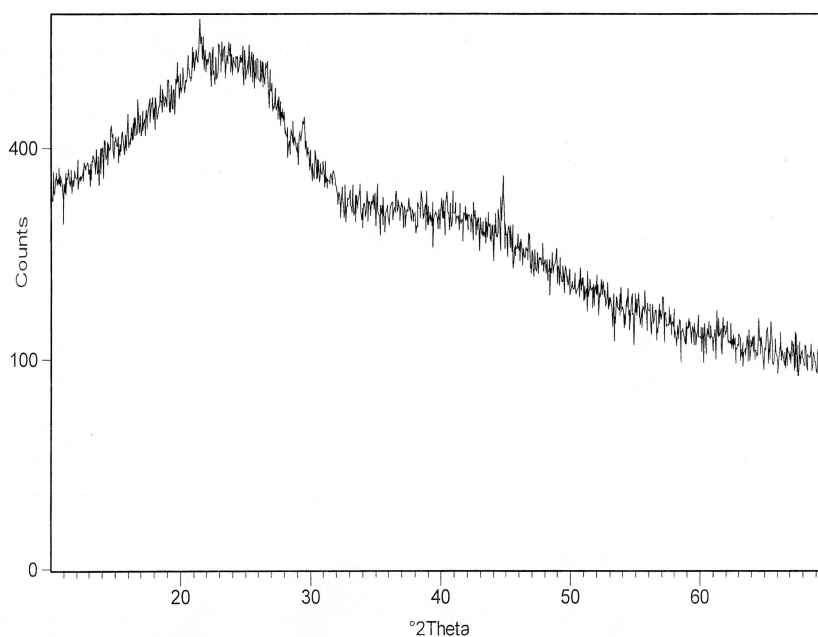


Fig. 3: X-Ray diffraction pattern of LS-1 sample.

The presence of large amount of organic matter and simultaneous presence of gypsum can be understood. This is because gypsum is precipitated in highly evaporating and humid conditions. This type of conditions is favorable for deforestation and hence favorable for the deposition of large amount of organic matter in sediments. This organic matter may be converted in coal or any other fossil fuel. Here it seems the condition for formation of coal was more favorable but from Mössbauer spectroscopic point of view it appears that there is correlation between presence of gypsum and presence of Jarosite.

It means presence of Jarosite may be used as geomarker for environmental conditions which are more favorable to deposit organic rich sediments (hematite).

The anomalous presence of Jarosite is expected in source rocks. Our argument is also supported by previous studies carried by Kulshreshtra *et al.* [11] and Tripathi *et al.* [12] on EKG and Cambay basins respectively, where they found appreciable amount of Jarosite in organic rich sediments. More studies are required to establish the correlation between presence of Jarosite and source rocks in petroliferous basin. Since this information is crucial (presence of source rocks) for hydrocarbon. So Mössbauer spectroscopy can be used as a tool for source rocks characterization.

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