



Full Paper

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Received: September 13, 2012

Accepted: December 28, 2012

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The identification of iron in a Spanish coal using low temperature Mossbauer spectroscopy (4.2°-40K)

Abstract

The method of using low temperature Mossbauer spectroscopy to identify the iron species in coal is illustrated for sub bituminous (AA5) and semi-anthracite (BZ) coals. The 4K spectrum of the AA5 sample exhibits besides pyrite and rozenite a magnetically split ferric component compatible with jarosite ($H = 485$ kOe). Whilst, set of low temperature spectra of the BZ sample, taken respectively at 9K, 20K, 30K and 40K indicate besides pyrite and szomolnokite other two relaxation sextets belong to siderite and ankerite. Furthermore, analysis of iron by the method of atomic absorption spectroscopy and according to ASTM methods for coal showed the presence of organically bound iron (0.133 % Fe.) in the BZ sample. The existent of an organic iron in a coal sample is of a great importance, which will be inevitably discussed in this work.

Key Words

Coal; Jarosite; Liquid helium; Ankerite; Mossbauer spectroscopy.

INTRODUCTION

In a previous paper^[2], the Mossbauer Effect at room temperature (RT) and 80 K in the sub-bituminous (AA5) and semi anthracite (BZ) coals has been described in some details. Iron was assigned therein as pyrite, rozenite and jarosite in the sub-bituminous sample and as pyrite, szomolnokite and siderite in the semi-anthracite one. The identification of the spectra corresponding to the different iron phases present in a coal sample is not often an easy task. As it is well known that there is strong overlapping of the sub spectra of the iron phases commonly encountered in coal. For example, although hyperfine parameters of pyrite and marcasite are very similar, a slight asymmetry in the pyrite doublet, which is usually the dominant component of the spectrum or isomer shift and quadrupole splitting values lower than those characteristic of pyrite can indicate the present of marcasite in the sample^[11]. The identification of siderite, illite and ferrous

sulphates can be possible in most of the cases because the peak at higher velocity usually appears sufficiently separated from the central peaks, but difficulties arise for the assignment of a determined hydrated ferrous sulphate form or for distinguishing ferrous sulphate (e.g. szomolnokite) from ferrous clay minerals/illite^[10]. The same problematic case is devoted for the assignment of siderite and ankerite. Hyperfine parameters of isomer shift = 1.23-1.28 mms^{-1} and quadrupole splitting = 1.78-2.09 mms^{-1} were identified for both at RT and/or 80 K^[10]. Therefore, either the use of other analytical techniques or the recording of low temperature Mossbauer spectra are mandatory. In this study, a low temperature (4.2 K) Mossbauer spectrum as well as series of spectra, taken at 9K to 40K are illustrated respectively for sub bituminous (AA5) and semi-anthracite (BZ) coals. The recording of low temperature Mossbauer spectra enabled us to confirm the RT identification of jarosite and siderite and yield a positive assignment for ankerite, which could

not identified in the room temperature BZ spectrum.

EXPERIMENTAL

Two Spanish coals, sub bituminous (AA5) and semi anthracite (BZ) have been chosen to carry out this work.

Low temperature mossbauer measurements

For Mossbauer experiments, disk shaped absorbers of 1 cm diameter and 0.3 mm thickness with about 300mg coal/cm² and sealed with a Styrofoam suspension. Mossbauer spectra were recorded at temperatures from 4.2K to 40 K, on a 1024 multichannel analyzer. The source is ⁵⁷Co in a rhodium matrix, kept at 300 K and moved in a constant acceleration mode with a maximum velocity calibrated at 10 mm/s. All Further details concerning experimental procedures and Mossbauer spectroscopy may be found in^[6]. All of the measured isomer shifts are quoted relative to natural iron at 300 K. The spectra were fitted with Lorentzian lines, assuming equal intensities and line widths for pairs of lines within magnetically split spectra and doublets. Iron phases were assigned according to references whereas indicated in the text.

“Organic” iron

TABLE 1 shows analysis of iron encountered in the BZ sample. Analysis was carried out according to ASTM methods for coal, which agrees with experimental procedure described by Lefelhocz et al^[9] and was obtained by atomic absorption spectroscopy. The nature of any organically iron in a coal sample is of a particular interest. As early as 1967, Lefelchcz et al^[9], tentatively assigned one of their iron spectra to organic iron, but this was subsequently determined to be a clay site. Previous details of Mossbauer Effect investigations [cf. Montano^[11,12]] on some US coals have not seen any evidence of organically bound iron. Schafer^[13] studied the oxidation of carboxylates in Victorian brown coal, Australia, but his report does not contain any details of the Mossbauer spectra or parameters obtained. However, based on ion exchange data, Durie^[8] suggested that the iron is ironically bound to carboxylate groups in the coal. In calculating equivalences between carboxylate content and exchangeable iron, it has been assumed that such iron is divalent^[1]. Cashion et al^[4] observed pyrite and a range of poorly resolved sites which they postulated were due to hydrolyses iron carboxylate of isomer shift = 0.25-0.5 mms⁻¹ and quadrupole splitting = 0.2-1.0 mms⁻¹. Although the iron analysis of BZ gives an estimation for organic iron, but the corresponding low temperature spectra over the range of 9 K to 40 K did not

indicate any organic site, probably because of its low abundant, (see TABLE 1).

TABLE 1 : Iron analysis (% Fe, Sample as received)

Total	HCl- Sol	Pyrite	"organic iron" by diff.
0.600	0.441	0.026	0.133

RESULTS AND DISCUSSION

AA5

Figure 1 shows a Mossbauer spectrum recorded on the AA5 absorber at 4.2K. Hyperfine Mossbauer parameters assigned to different iron phases are given in TABLE 2. Guided by the shape of the spectrum we fitted it by superimposing of three components: a sextet due to magnetically ordered iron (labelled J), an intense central doublet (P) and a second doublet with large quadrupole splitting (R). The respective phases are jarosite, pyrite and rozenite. As it could be expected: at liquid helium temperature pyrite and rozenite still show a doublet, whilst the spectrum of jarosite is magnetically split whose hyperfine field is 485 kOe, (see again figure 1). The previous finding of jarosite as a paramagnetic doublet at RT and here as a sextet inferred its superparamagnetism. Cook and Cashion^[5] have reported that superparamagnetism is a phenomenon peculiar to ultra fine particles of magnetically ordered material in which the anisotropy energy (KV) barrier between ‘easy’ directions of magnetization is comparable with the thermal energy $k_B T$, so that a particle’s magnetization can flip from one direction to another. If this flipping is sufficiently rapid, (i.e. the particle is sufficiently small), the magnetic hyperfine field at the iron nucleus effectively averages to zero on a Mossbauer timescale and consequently doublet spectrum rather than magnetic sextet is obtained.

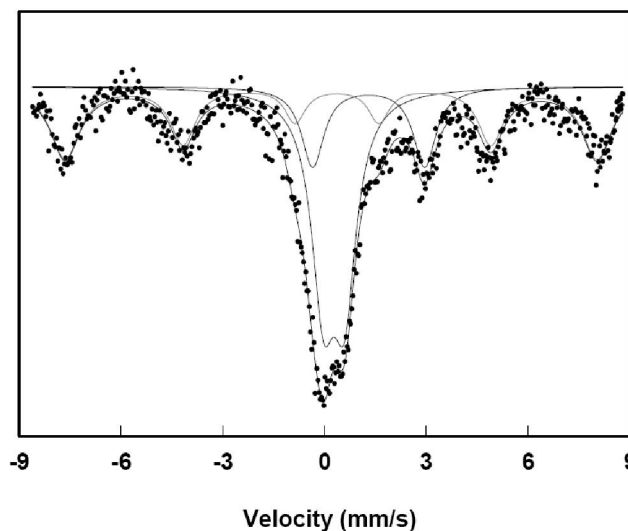


Figure 1 : Mossbauer spectrum of the AA5 coal sample at 4.2 K. Points-the data, full line-the best fit to the data.

TABLE 2 : Mossbauer hyperfine data for the AA5 and BZ coals at low temperatures.

Sample	T K	Fe Phases	δ_{Fe} mms ⁻¹	ΔE_Q mms ⁻¹	H_{eff} kOe	Γ	Assignment
AA5	4.2	J	0.28	-0.17	485	0.74	Jarosite
		P	0.28	0.63	-	0.81	Pyrite
		R	1.30	3.31	-	0.82	Rozenite
BZ	9	1	1.33	2.09	184	0.39	Fe/Mg CO ₃
		2	1.66	2.12	148	0.45	Ankerite
		S	1.39	2.19	-	0.53	Szomolnokite
		P	0.12	0.44	-	0.62	Pyrite
BZ	20	1	1.25	2.07	186	0.32	Fe/Mg CO ₃
		2	1.53	2.31	147	0.32	Ankerite
		S	1.30	2.14	-	0.56	Szomolnokite
		P	0.04	0.49	-	0.43	Pyrite
BZ	30	1	1.27	1.96	-	0.35	Fe/Mg CO ₃
		2	0.96	1.78	174	0.35	Ankerite
		S	1.16	2.87	-	0.30	Szomolnokite
		P	0.12	0.32	-	0.53	Pyrite
BZ	40	1&2	1.24	2.03	-	0.33	*Sidrite
		S	1.32	2.39	-	0.41	Szomolnokite
		P	0.07	0.62	-	0.44	Pyrite

Errors: $\delta_{Fe} \pm 0.06 \text{ mms}^{-1}$; $\Delta E_Q \pm 0.03 \text{ mms}^{-1}$; $H \pm 8 \text{ kOe}$; $\Gamma \pm 0.03 \text{ mms}^{-1}$; Chi Squares were 0.685×10^{-3} for AA5 and $\sim 0.573 \times 10^{-3}$ for BZ spectra (an average); * same as reported in^[2].

BZ

Likewise, figure 2 shows series of low temperature spectra, recorded on the BZ absorber. Temperatures at which spectrum is measured are indicated (9K-40K). Hyperfine parameters assigned to each phase are summarized again in TABLE 2. In general, these low temperature spectra are a plausible meaning of relaxation. Most authors (cf. Ahmed et al.^[3]) have assumed an exponential temperature dependence of the relaxation time (τ) as:

$$\tau = \tau_0 \exp(KV/K_B T)$$

τ_0 is the order of 10^{-10} s; KV is the energy barrier to be overcome the direction change of the magnetization with anisotropy energy density K and for a particle of volume V; K_B is a Boltzman's constant, and T is the temperature. Below the blocking temperature, the relaxation time is long compared to the nuclear larmor precession period, "slow" ($10^{-8} \text{ s} < \omega_L^{-1} < 10^{-7} \text{ s}$), and in this case, a magnetic split sextet will be observed. Above the blocking temperature, the magnetic sextet collapse and completely vanishes because of "fast" relaxation, so that the quadrupole splitting doublet will shows up in the spectrum.

As it could be justified in figure 2, both spectra at 9K and 20K, are well described by a superposition of: two 'slow' relaxation components (1&2) besides szomolnokite (S) and pyrite (P). These two components gave hyperfine

Mossbauer parameters close to $\text{Fe}^{2+}/\text{MgCO}_3$ ^[14] and Fe^{2+} in ankerite^[7] respectively. At 30K, only quadrupole splitting of $\text{Fe}^{2+}/\text{MgCO}_3$ is obtained whilst an overlapped doublet similar to that obtained at RT was observed at 40K for both. Furthermore, Srivastava^[14], made a systematic Mossbauer observation of paramagnetic hyperfine spectra of $\text{Fe}^{2+}:\text{MgCO}_3$ at liquid helium temperatures ($T < 50\text{K}$) due to slow spin-lattice relaxation rates. Whilst, at higher temperatures above 50K, the spin-lattice relaxation rate becomes very fast ($\tau \gg \omega_L$), and consequently only a pure quadrupole splitting is observed. Ahmed et al.^[2] have noticed that substitution of Fe by other cations such as Ca, Mg and Mn results in a distortion of the symmetry around the iron atoms, which reduces the quadrupole splitting of pure siderite FeCO_3 at RT from 1.8 mms^{-1} to 1.69 mms^{-1} . Accordingly, the Mossbauer values obtained for component (1) was assigned to Fe/MgCO_3 . On the other hand, the second component exhibits an effective magnetic field of 173 kOe, which ascribed the 'slow' spin-orbit relaxation of the ferrous iron in ankerite. This result is in agreement with those reported by De Grave^[7], who was estimated an average effective hyperfine field of 175 kOe obtained by fitting lorentzians to experimental spectra performed for natural ankerite sample, at liquid helium temperatures and in an external applied field of 60 kOe. The approximate composition was $(\text{Ca}_{1.1}\text{Mg}_{0.5}, \text{Fe}_{0.5} \text{Mn}_{0.5}) (\text{CO}_3)_2$.

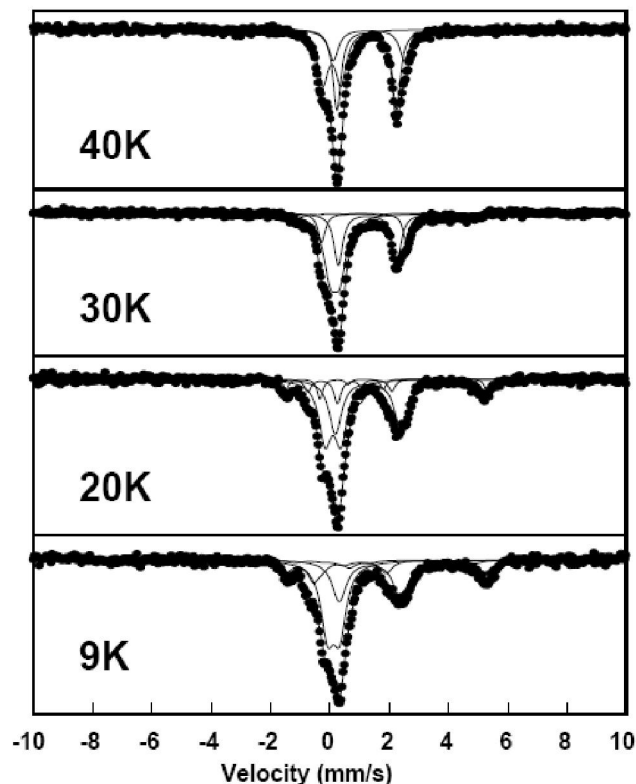


Figure 2 : Mossbauer spectra of the BZ coal sample at low temperatures (9K-40K). Points-the data, full line-the best fit to the data.

Finally, word of quotation has to be made that observation of pure quadrupole splitting of $\text{Fe}^{2+}/\text{MgCO}_3$ at 30K does not on the line of those reported by Srivastava^[14], who claimed that a quadrupole splitting for $\text{Fe}^{2+}\text{MgCO}_3$ is obtained at $T > 50\text{K}$. This disagreement presumably is related to the volume of $\text{Fe}^{2+}\text{MgCO}_3$ grains. When they are sufficiently small to add an excess to the relaxation, the detection of quadrupole splitting at temperatures below 50 K is possible. In summary, low temperature Mossbauer measurements allowed us to confirm the RT identification of jarosite and siderite and yield a positive assignment for ankerite, which could not be identified in the room temperature BZ spectrum because of fast relaxation. It exhibits as a very relaxation magnetic split at liquid helium temperatures (9K-30K).

ACKNOWLEDGMENT

The author is indebted to Profs. R.E.Vandenberghe, and E. De Grave, (Department of Physics, Faculty of Sciences, Ghent state University, Ghent, Belgium, for their cooperation in the low temperature Mossbauer measurements and helpful discussion.

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