MOSSBAUER ANALYSIS ON THE MICROWAVE—MAGNETIC DESULFURIZATION OF RAW COAL

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ABSTRACT

The selective dielectric heating of microwave energy to convert a portion of each pyrite particle to moderately magnetic pyrrhotite has been suggested to enhance the magnetic separation of inorganic sulfur from coal. The results for Mossbauer analyses show that the considerable amount of pyrrhotite produced during microwave irradiation, carrying with it some of non–magnetic pyrite (unconverted), ferrous sulfate, and troilite, is completely removed from coal after magnetic separation. The optimum desulfurization efficiency can be attained by appropriately controlling the irradiation time to maximize the amount of pyrrhotite formed pyrite decomposition. Excessive irradiation would be disadvantageous for improving magnetic separation due to the further decomposition of pyrrhotite to antiferromagnetic troilite.

Keywords: Coal desulfurization　Microwave irradiation　Magnetic separation Mossbauer spectroscopy

1　INTRODUCTION

Sulfur occurs in coal in three forms: the inorganic, the organic, and the trace elemental sulfur, which release SO_2 into the atmosphere and corrode metallic equipment upon combustion and conversion of coal. Consequently, the utilization of coal, as the most important fuel and the chemical raw material, strongly requires development of technically feasible and economical means for sulfur removal from raw coal.

The physical methods of coal cleaning act principally upon the inorganic sulfur largely as pyrite. In general, the separation depends on differences between coal and sulfur–bearing minerals in densities or in magnetic susceptibilities. However, the popular density difference techniques, such as employing heavy media and froth floatation, can not remove finely disseminated pyrite microcrystals from coal. The high–gradient magnetic separation (HGMS) technique is also difficult in practice

because the difference in magnetic susceptibilities is extremely small[1]. Ergun and Bean first proposed, in an early review of magnetic depyriting of coal, that high–frequency heating of coal might result in selective absorption by pyrite. They noted that conversion of only 1 % of pyrite (FeS_2) to its neighboring sulfide, pyrrhotite ($Fe_{1-x}S$, $0 < x \leqslant 0.125$), would be accompanied by a major increase in susceptibility[2]. For the past fifteen years, more intensive efforts at high–frequency heating for coal desulfurization have been carried out in America[3–8].

The aims of current study were to examine the influence of irradiation time on the microwave–magnetic desulfurization of coal and to explore the optimum condition for removing as much inorganic sulfur from coal as possible. For this purpose ^{57}Fe Mossbauer analyses were made to detect the transformation of Fe–S compounds in coal during microwave irradiation and subsequent magnetic separation.

2   EXPERIMENTAL DETAILS

The bituminous coals with high pyritic sulfur content from southwest China was employed in present investigation. All the coal samples were finely pulverized to < 100 mesh and stirred to the full extent in order to improve their homogeneity. The amount of coal sample used for irradiation experiment was approximately 10 g.

Microwave irradiation treatments were carried out at 2.45 GHz in the TE_{10n} mode rectangular cavity reactor with nitrogen gas. The power level was about 1.5 kW and the irradiation treatment time was 30, 60, 80 and 100 s, respectively.

After microwave exposure, a portion of each irradiated coal sample was selected for the Mossbauer measurement, the remainder was magnetically separated into both magnetic and non–magnetic fractions using a hand–held magnet of 0.6 T. Next the Mossbauer spectra of both fractions were recorded.

The Mossbauer spectrometer used was a conventional constant–acceleration spectrometer. The source consisted of 1.48×10^9 Bq of ^{57}Co in a Rh matrix. All spectra were recorded at room temperature (RT) and fitted with least–squares method. The isomer shifts were calculated with respect to α–Fe at RT.

3   RESULTS AND DISCUSSION

The Mossbauer spectra for raw coal samples, microwave–irradiated coal samples, and their magnetic and non–magnetic fractions are shown in Figs.1—4, respectively. The relative Mossbauer absorption for various iron phases in samples are compiled in Table 1 and their Mossbauer parameters are listed in Table 2.

The inorganic sulfur occurs in raw coal mainly in pyritic and sulfate forms. Mossbauer spectra shown in Fig.1 indicate that pyrite (FeS_2) is the dominant sulfur–bearing mineral in sulfur–rich coals, and that sulfates, such as szmolnokite

(FeSO$_4$ · H$_2$O), jorosite (KFe$_3$(SO$_4$)$_2$(OH)$_6$), and anhydrous ferrous-sulfate (FeSO$_4$), formed by oxidation of pyrite veneering on the pyrite particles during coal weathering, are present at a low concentration. The disulfide, pyrite FeS$_2$, has a

Table 1

Mossbauer analyses of various Fe—S compounds in samples   %

Spectrum	FeS$_2$	FeSO$_4$ · H$_2$O	KFe$_3$(SO$_4$)$_2$(OH)$_6$	FeSO$_4$	A	B	C	FeS
			Mossbauer spectral area			Fe$_{1-x}$S		FeS
Fig.1a	81	12	7	–	–	–	–	–
Fig.1b	87	–	–	13	–	–	–	–
Fig.2a	76	–	–	11	4	5	4	–
Fig.2b	38	–	–	3	14	16	15	14
Fig.2c	9	–	–	–	10	10	8	63
Fig.2d	3	–	–	–	6	5	5	81
Fig.3a	38	–	–	–	20	23	19	–
Fig.3b	32	–	–	4	15	18	16	15
Fig.3c	15	–	–	–	22	23	17	23
Fig.3d	8	–	–	–	25	23	21	23
Fig.4a	86	–	–	14	–	–	–	–
Fig.4b	100	–	–	–	–	–	–	–
Fig.4c	4	–	–	–	–	–	–	96
Fig.4d	–	–	–	–	–	–	–	100

NaCl-type cubic lattice, in which the ferrous cations and the [S-S]$^{2-}$ complex anions are placed in the A sites and the B sites, respectively; and gives the lower values of both isomer shift IS and quadrupole splitting QS (IS = 0.31 mm / s, QS = 0.61 mm / s, see Table 2), suggesting that these ferrous cations are in the low spin configuration (T$_{2g}^6$e$_g^0$). Under the action of strong ligand field of the [S-S]$^{2-}$ complex anions, the six d-electrons of ferrous cation are completely occupying the T$_{2g}$ ground state orbits and the ferrous cation bonds with the octahedral coordination complex anions [S-S]$^{2-}$ through the d^{2}sp^3 hybridization. Consequently pure pyrite is not magnetic. By the way, the above-mentioned sulfates are paramagnetic at room temperature (the

Table 2

Mossbauer parameters of Fe—S compounds in samples*

Fe-S compound		IS /mm · s^{-1}	QS /mm · s^{-1}	B /T
FeS$_2$		0.31	0.61	—
FeSO$_4$ · H$_2$O		1.25	2.73	—
KFe$_3$(SO$_4$)$_2$(OH)$_6$		0.35	1.22	—
FeSO$_4$		1.26	2.89	—
Fe$_{1-x}$S	A	0.70	0.06	30.2
	B	0.71	0.05	27.6
	C	0.69	0.08	25.4
FeS		0.77	-0.06	31.3

* Isomer shift IS with respect to α-Fe at RT. Quadrupole splitting QS = [(v_6- v_5)- (v_2- v_1)]/4 for hyperfine field B≠0

antiferromagnetic–ordering temperature 4—15 K)[9]. On the other hand, "clean coal" (without other mineral matter) is weakly diamagnetic. Thus, even though coal was pulverized sufficiently to liberate pyrite particles, the magnetic separation of inorganic sulfur from coal is also very difficult.

It is of interest to note that microwave electromagnetic energy can be preferentially deposited at pyrite–bearing areas of coal[4,5]. The localized high temperature produced by selective dielectric heating of microwave energy can induce thermochemical, in situ, reactions between pyritic sulfur and other neighbouring reactive constituents present in coal[3]. From Mossbauer spectra of microwave–irradiated coal samples (Fig.2a—d), it may be seen that the disulfide (FeS_2) is converted monosulfides both pyrrhotite ($Fe_{1-x}S$) and troilite (FeS) during microwave irradiation, and that the in situ thermodecomposition reactions of pyrite in coal
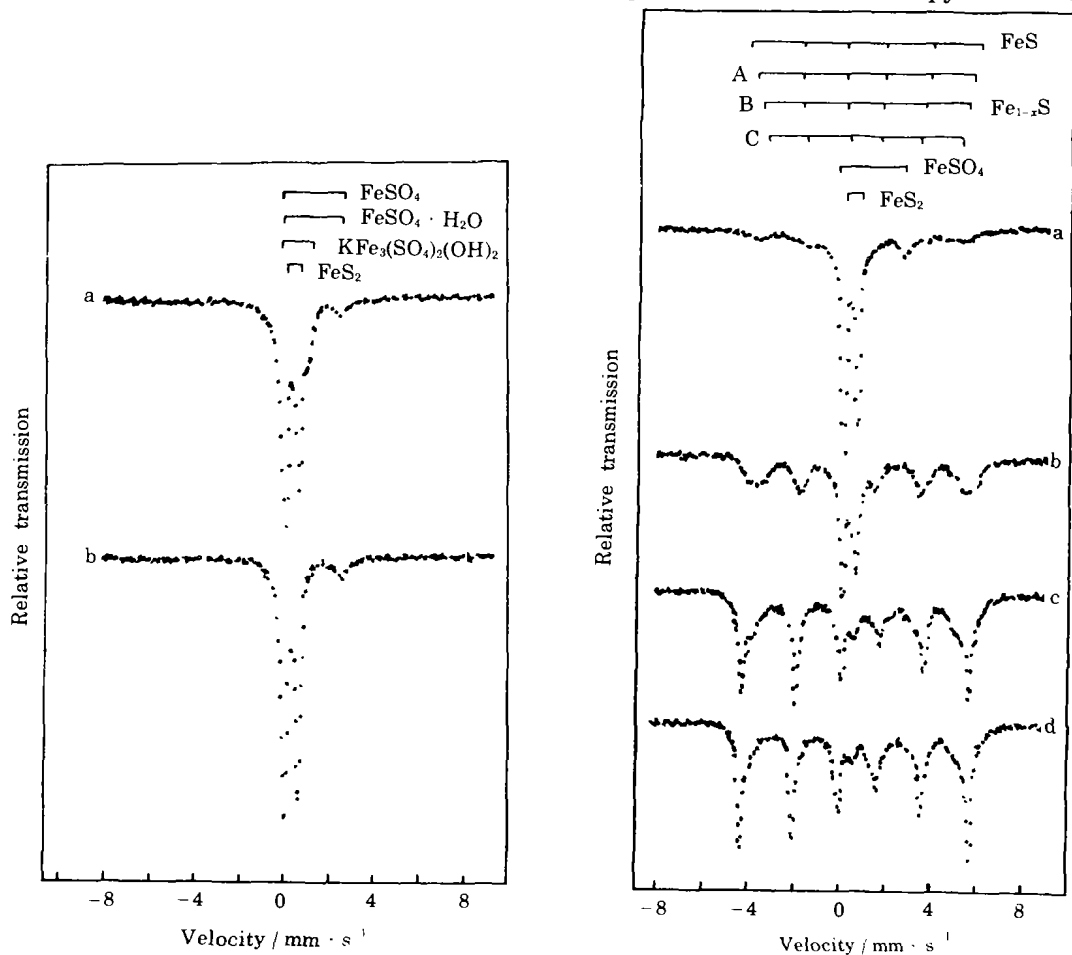

Fig.1   Mossbauer spectra of bituminous coals with high sulfur content

(a) Coal sample B–1   (b) Coal sample B–2

Fig.2   Mossbauer spectra of coal sample B—2 after microwave irradiation

Irradiation time: (a) 30 s (b) 60 s (c) 80 s (d) 100 s

grains, $FeS_2 \rightarrow Fe_{1-x}S \rightarrow FeS$, consecutively progress towards the right with increasing

irradiation time. The monosulfides ($Fe_{1-x}S$, FeS) appear as a surface coating on the pyrite particles, and the sulfur–iron atomic–ratio across the pyrite particle changes from 2 (corresponding to FeS_2) to 1 (corresponding to FeS)[8].

In Fig.2a—d the Mossbauer spectra of all the monosulfides exhibit the magnetic ordering. The stoichiometric FeS has the NiAs–type 2C superstructure below T_a (= 420 K), in which the ferrous cations are octahedrally surrounded by S^{2-} anions through the sp^3d^2 hybrid orbits and are in the high spin configuration ($T_{2g}^4 e_g^2$) owing to
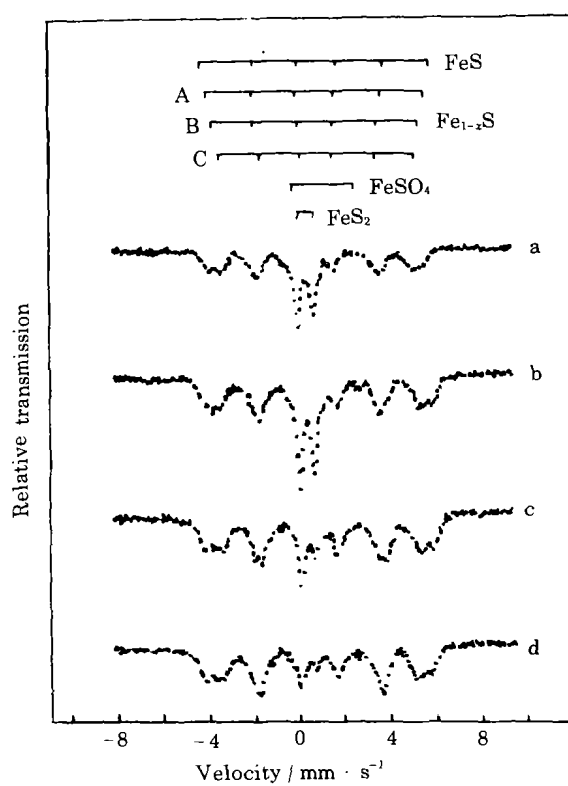

Fig.3 Mossbauer spectra of the magnetic fractions of coal sample B—2 after microwave irradiation

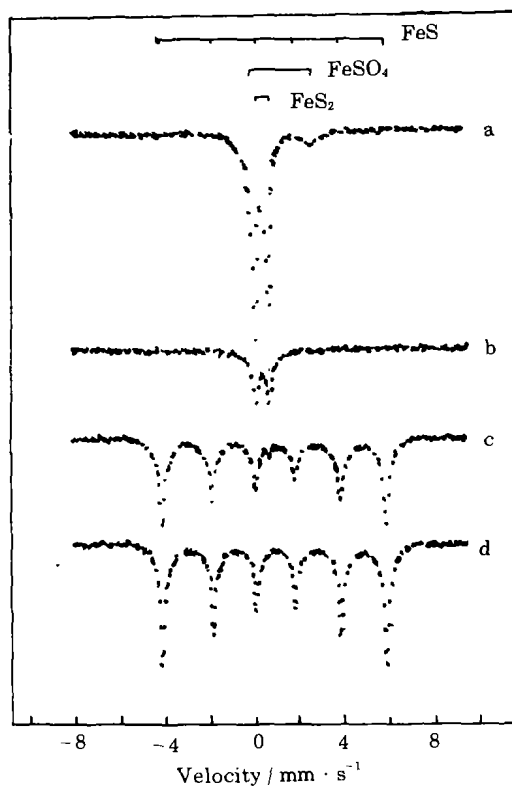Irradiation time: (a) 30 s (b) 60 s (c) 80 s (d) 100 s

Fig.4 Mossbauer spectra of the non—magnetic fractions of coal sample B—2 after microwave irradiation

Irradiation time: (a) 30 s (b) 60 s (c) 80 s (d) 100 s

weakening of strength of ligand field of S^{2-} anions. There is a ferromagnetic exchange interaction between the ferrous cations in the C–plane, while the ferrous cations on adjacent C–planes have superexchange antiferromagnetic interaction through the intervening sulfur anions and the net magnetic moment is zero. Consequently troilite

is antiferromagnetically ordered[10,11], its Mossbauer spectrum exhibits a single sixtet with a finite value of magnetic hyperfine field (B = 31.3 T), corresponding to antiferromagnetically ordered iron in only one site in the structure. The Neel temperature of FeS is 593 K. The family of nonstoichiometric pyrrhotites with varied compositions has long been ascribed to a deficiency of ferrous cations in the NiAs-type structure, and the cation vacancies apparently play a leading role in the control of the magnetic susceptibility[11]. Especially, the 4C superstructure of $Fe_{0.875}S$ (i.e., Fe_7S_8), on the basis of Bertaut model[12], contains 12.5 % ordered cation vacancies, all of which are confined to one of two negatively coupled equivalent sublattices. This results in the greatest imbalance of the sublattices and consequently the strongest ferrimagnetism, and the symmetry of the system is thereby lowered from the hexagonal $D_{3h}^4 - C_{62c}$ space group of FeS to the monoclinic space group $C_{2h}^6 - C_{2/c}$. The magnetic hyperfine field differs considerably between the different iron sites in the pyrrhotites, and is reduced with an increase in the number of nearest neighbor vacancies[11]. The average magnetic hyperfine field B is given by $B = (1/A)\Sigma_n A_n B_n$, where A is the sum of each subspectral area A_n, and B_n the magnetic hyperfine field due to nth site. The average stoichiometry of pyrrhotites can be determined according to: at.% Fe = 100 × [0.6836 × 10^{-2} × B + 0.2881][13]. It is easily found from the spectral parameters (Table 1 and 2) that the atomic percent iron (at.% Fe) in pyrrhotites in samples is 47.74— 47.89, average value 47.82, corresponding to the stoichiometric formula $Fe_{0.9166}S$.

As stated above, the selective dielectric heating of microwave energy can convert a portion of each non-magnetic pyrite particle to a more magnetic form, and hence magnetic separation of inorganic sulfur from coal would be facilitated. The Mossbauer spectra of non-magnetic fractions of microwave-irradiated coal samples (Figs.4a—d) confirmed that no trace of pyrrhotite is observed. For both more particular states, i.e., microwave treatment for 60 or 100 s, only the pyrite or the troilite are retained in their non-magnetic fraction (Figs.4b, d). Therefore, it is safe to say that the considerable amount of pyrrhotite produced during microwave treatment has been completely separated into the magnetic fraction after magnetic separation. On the other hand, from the Mossbauer spectra of magnetic fractions (Figs. 3a—d), some of non-magnetic FeS_2 (unconverted), FeS, and $FeSO_4$ were also carried by $Fe_{1-x}S$ to the magnetic fraction. Jacobs et al. confirmed from experimental results that the sensitivities of the 14.4 keV γ-ray resonant absorption for FeS_2, $Fe_{1-x}S$, and FeS were essentially equivalent[6]. Therefore, it can be postulated that the Debye-Waller factors for all the Fe-S compounds in samples are the same. In this approximation, the formula for estimating the inorganic desulfurization efficiency resulting from the combination of microwave irradiation and magnetic separation is given as follows:

$$\eta = 1 - [\Sigma_j A_j S_j - (A' / A'') \Sigma_k A_k S_k] / \Sigma_i A_i S_i$$

where, A_i is the percentage spectral area of each Fe–S compound in the raw coal sample (Fig.1) and S_i is the amount of sulfur atoms per iron atom in each of these compounds, respectively; A_j, S_j and A_k, S_k are the corresponding values for each of the microwave–irradiated coal samples (Fig.2) and for its magnetic fraction (Fig.3), respectively; A' and A'' is the sum of each subspectral area percentage of $Fe_{1-x}S$ in each of the microwave–irradiated coal samples and in its magnetic fraction, respectively. For coal sample B–2 corresponding to irradiation time of 30, 60, 80 and 100 s, from the above formula, the η value is 21 %, 91 %, 69 % and 58 %, respectively. Judging from this, the enhancement of magnetic separation of inorganic sulfur from coal after microwave treatment is very obvious.

It will be seen from above experimental results that the influence of irradiation time on magnetic separation of inorganic sulfur from coal is certainly present. The optimum desulfurization efficiency can be attained by controlling properly the irradiation time to maximize the amount of pyrrhotite formed from pyrite decomposition during microwave treatment. Excessive irradiation time would be disadvantageous for improving magnetic depyriting due to the further decomposition of pyrrhotite to antiferromagnetic troilite.

The microwave–magnetic desulfurization is an attractive, novel and efficient physical method of coal cleaning. Selectively changing microwave treatment condition to an optimum to generate a higher magnetic substance, such as Fe_7S_8, $\gamma-Fe_2O_3$, or Fe_3O_4, is a subject worthy of further research.

ACKNOWLEDGMENTS

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