

TRACKING PYRITIC SULFUR DURING THE MICROWAVE—CHEMICAL DESULFURIZATION OF COAL USING MOSSBAUER SPECTROSCOPY

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ABSTRACT

The transformations of pyrite in coal during the microwave—chemical treatment for desulfurization of coal was studied with Mössbauer spectroscopy of ^{57}Fe . The results for phase analyses show that the selective dielectric heating by microwave energy can give rise to the thermal decomposition of pyrite FeS_2 in coal to new phases, pyrrhotite Fe_{1-x}S ($0 < x \leq 0.125$) and troilite FeS which can be dissolved in dilute HCl solution. Therefore the microwave irradiation combined with the acid washing treatment will be an effective method of desulfurization of coal.

Keywords: Coal Desulfurization Microwave irradiation Acid-washing Mössbauer spectroscopy

1 INTRODUCTION

Coal is one of the most readily available energy resources, but it is also the greatest source of air pollution in China. Troublesome environmental problems arise from its sulfur-containing constituents which release SO_2 into the atmosphere and corrode metallic equipments upon the combustion of coal. There are a variety of physical, chemical and microbiological methods for precombusting desulfurization of coal under development and a few are in use. A possible method is the preferential dielectric heating of the pyrite if the dielectric properties of pyrite and coal are sufficiently different so that the pyrite will absorb more electromagnetic energy and heat faster than the coal and hence can be self-decomposed. The aims of this paper were to determine the transformations of pyrite in coal in the microwave treatment process and in the subsequent acid-washing treatment process, and to calculate the desulfurization rate of inorganic-sulfur in coal.

2 EXPERIMENTAL

The coal used in this study is Sichuan bituminous coal which contains 2.83wt %

inorganic sulfur, of which the amount of sulfate is rather small and is not important. 50 g of coal samples were finely ground to pass a 100 mesh sieve in order to improve

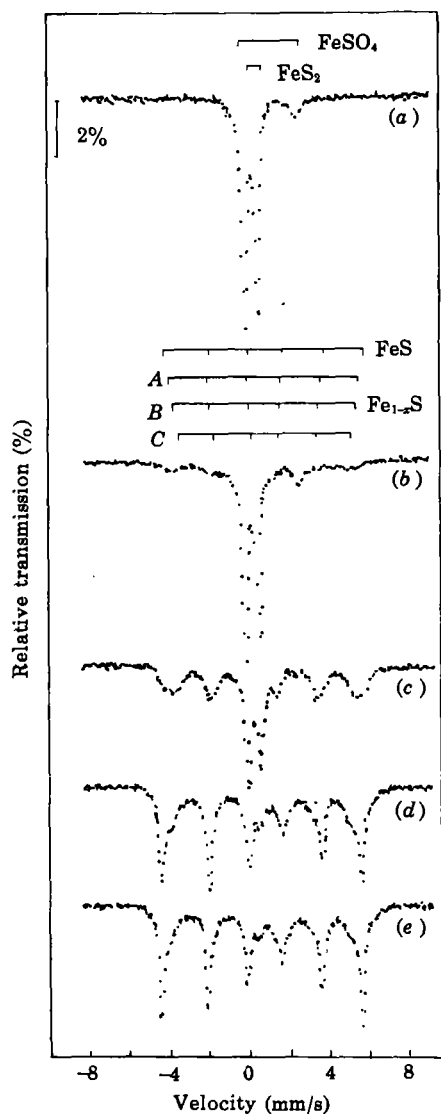


Fig.1 Mössbauer spectra of coal samples for various irradiation time

(a) Before (b) 30 s (c) 60 s (d) 180 s (e) 100 s

Mössbauer spectra of coal samples for various irradiation times are shown in Fig.1 and their Mössbauer analyses are given in Table 1.

The Mössbauer spectrum shown in Fig.1a indicates that the pyritic sulfur is the dominant form of sulfur occurring in sulfur-rich coals. In general, the presence of

its homogeneity. each 10 g of coal samples for every run was loaded into a quartz crucible (ϕ 38 mm \times 48 mm) and located at a place in the TE_{10n} mode rectangular cavity resonator where the microwave electrical field intensity is maximal. After admitting nitrogen gas, the coal samples were irradiated with microwave energy at 2.45 GHz at power level of about 1.5 kW for 30, 60, 80 and 100 s, respectively.

After the microwave treatment, 1 g of each above-mentioned four irradiated coal samples was selected for the Mössbauer measurement, respectively. Additionally, each 5 g of these irradiated coal samples were mixed with 100 ml of 5% HCl solution and the resulting slurry was boiled for more than 30 min, then filtered and thoroughly washed with distilled water, the dried samples then were analyzed, respectively.

Mössbauer spectra of the above-mentioned coal samples were obtained at room temperature by using conventional spectrometer and fitted by computer. The zero velocity is given in reference to α - Fe.

3 RESULTS AND DISCUSSION

3.1 The transformations of pyrite in coal during microwave irradiation

ferrous sulfate FeSO_4 at a lower concentration in coal has been considered to be formed by oxidation of pyrite and is an indication of weathering. Fe^{2+} ions in ferrous sulfate have a more positive isomer shift ($\text{IS}=1.26 \text{ mm/s}$), which is indicative of a highly ionic compound. By contrast, the values of isomer shift (IS) and quadrupole splitting (QS) for pyrite (see Table 1) show the covalent bonding between the 6-coordinated Fe_6^{2+} cations and the $[\text{S}_2]^{2-}$ anionic complexes in its cubic lattice. Therefore, the former can be dissolved in dilute HCl solution, whereas the latter can not, as stated in the analysis procedure of ASTM-D2492.^[1]

Table 1

Mössbauer analyses of Fe-S compounds in coal samples for various irradiation time

Fe-S compound	IS (mm/s)	QS (mm/s)	H ($10^6/4\pi$ A/m)	Mössbauer spectral		area (%)			
				Fig.1a	Fig.1b	Fig.1c	Fig.1d	Fig.1e	
FeS_2	0.31	0.61	—	87	76	38	9	3	
Fe_{1-x}S A	0.70	0.06	302	—	4	14	10	6	
B	0.71	0.05	276	—	5	16	10	5	
C	0.69	0.08	254	—	4	15	8	5	
FeS	0.77	-0.06	313	—	—	14	63	81	
FeSO_4	1.26	2.89	—	13	11	3	—	—	

IS, QS and H values given are means of all observation, IS relative to α -Fe at RT, $\text{QS}=[(V_6-V_3)-(V_2-V_1)]/4$ for $H \neq 0$

Besed on Fe-S system phase diagram, the self-decomposition of pyrite requires high-temperature above 700°C .^[2] Bommannavar *et al.* studied the decomposition of pyrite in coal in a nitrogen atmosphere using in-situ ^{57}Fe Mössbauer spectroscopy, and observed the transformation of pyrite in coal to pyrrhotite commencing at 300°C .^[3] It follows that the $\text{FeS}_2/\text{Fe}_{1-x}\text{S}$ in coal reacts with the coal constituents. However the problem in heating pyrite in coal is that the coal will also be heated. This could result in pyrolysis of the coal matrix. Fanslow *et al.* obtained from experimental dielectric heating of coal and pyrite mixtures at 2.45 GHz that pyrite heated approximately nine times faster than 'clean coal' ^[4]. Hence the use of selective dielectric heating by microwave energy to heat the pyrite will not give rise to the significant evolution of hydrogen or carbon containing matter whose evolution would result in loss of the heating value of coal.

It may be seen from Fig.1b-e that the inherent pyrite FeS_2 in coal is transformed to new phases, pyrrhotite Fe_{1-x}S ($0 < x \leq 0.125$) and troilite FeS ; and that the decomposing reaction, $\text{FeS}_2 \rightarrow \text{Fe}_{1-x}\text{S} \rightarrow \text{FeS}$, will successively progress toward the right with increase of the irradiation time.

The magnetic hyperfine field H differs considerably between the different iron sites in the pyrrhotite, and is reduced as the number of nearest neighbour vacancies increases. The atomic percentage of Fe in Fe_{1-x}S can be calculated according to:

$$\text{at}\% \text{ Fe} = 100[0.6836 \times 10^{-3} \times \bar{H} + 0.2881]$$

The average magnetic hyperfine field $\bar{H} = (1/A) \sum_i A_i H_i$, where A is the sum of each subspectral area A_i ; and H_i the magnetic hyperfine field due to i -th site^[3,5,6]. The calculated results from the spectral parameters show that at% Fe in Fe_{1-x}S (Fig.1b-e) is 47.74–47.89, average value 47.82, and the corresponding stoichiometric formula $\text{FeS}_{1.091}$.

3.2 The acid– washing treatment after microwave irradiation

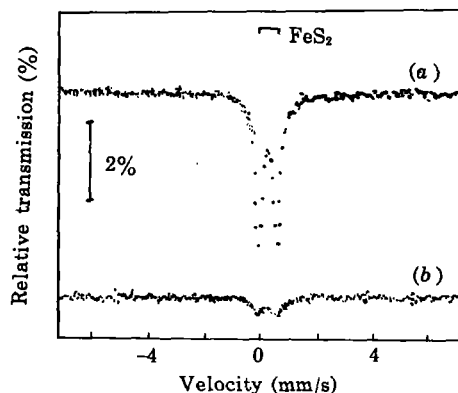


Fig.2 Mössbauer spectra of coal samples after HCl treatment

Irradiation time: (a) 30 s (b) 100 s

Therefore these Fe–S compounds can be solved in dilute hydrochloric acid solution which allows sulfur to be liberated upon the forming of hydrogen sulfide. The Mössbauer spectra of acid–washed coal samples after irradiation treatment indicate that Fe_{1-x}S , FeS and FeSO_4 are absent and that only the HCl–insoluble FeS_2 which has not been decomposed up to the end of microwave irradiation is remained (see Fig.2).

Jacobs *et al.* confirmed that the sensitivities of the 14.4 keV gamma–ray resonant absorption for FeS_2 , Fe_{1-x}S and FeS were essentially equivalent^[7]. It is therefore, a good approximation that their recoilless fraction for ^{57}Fe are similar. In this approximation, we obtained the desulfurization rate for inorganic–sulfur resulting from the microwave–chemical treatment:

$$\eta = 1 - A_r S_r / \sum_n A_n S_n$$

where A_n is the percentage spectral area of each Fe–S compound in raw coal (Fig.1a) and S_n is the amount of sulfur atoms per Fe atom in each of these compounds; the A_r , S_r are the corresponding values of FeS_2 in microwave treated coal samples (Fig.1b–e), i.e., of residual FeS_2 after acid–washing, $S_r = 2$.

The HCl–soluble Fe–S compounds increase in irradiated coal samples and the

Over the process of microwave desulfurizing reaction, the bulk S^{2-} ions in pyrite particles diffuse successively toward the surface, reconstructing the lattices from the cubic (FeS_2) to the hexagonal (Fe_{1-x}S , FeS) and accompanying simultaneously with change of the bonding property between the iron and the sulfur atoms. From analyzed results of spectra (see Table 1) the values of isomer shift for new phases, pyrrhotite and troilite, markedly increase by contrast to pyrite. It reveals that the percentage density of ionic bond in hexagonal lattice is greatly enhanced.

desulfurization efficiencies for the microwave-chemical treatment are enhanced obviously with increase of the irradiation time. From Mössbauer parameters and spectral areas, readily obtain that the above-mentioned inorganic desulfurization rates for irradiation time of 30, 60, 80 and 100 s are 19%, 59%, 90% and 97%, respectively. Almost all of the inherent inorganic-sulfur in coal can be removed by increasing moderately the microwave irradiation time to enable the decomposing reaction of FeS_2 to the fullest and by combining with the subsequent acid-washing treatment.

Consequently, the microwave-chemical treatment is an attractive, novel and efficient method for coal cleaning.

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