

INVESTIGATION OF VIRGIN COALS AND COALS SUBJECTED TO A MILD ACID TREATMENT

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A quantitative determination of the relative marcasite/pyrite contents in virgin coals is possible by means of ⁵⁷Fe Mössbauer spectroscopy. Complications arise, however, when iron-containing silicates, carbonates, or other salts are present. The application of a mild chemical treatment involving hydrofluoric acid has been employed to remove these Fe-containing phases while leaving the iron-disulfide phases unaffected.

Several South African coal samples with non-iron disulfide, Fe-containing phases ranging from 18 to 30 weight percent have been subjected to a hydrofluoric acid leaching at room temperature. The loss of mineral matter with HF leaching correlates well with the mineral matter residue following low temperature ashing. The ⁵⁷Fe Mössbauer spectra of the resulting coal samples, collected at 297K, indicate that only FeS₂ phases are present. The Mössbauer parameters for these samples ($0.619 \leq EQ \leq 0.622 \text{ mm s}^{-1}$; $0.306 \leq \delta \leq 0.309 \text{ mm s}^{-1}$) indicate the absence of appreciable quantities of marcasite in the coals. These Mössbauer parameters differ slightly, but systematically, from those of pyrite for which a quadrupole splitting of $0.6110 \pm 0.0020 \text{ mm s}^{-1}$ has been established. On the basis of previous studies, these increased EQ values suggest the presence of As substitution in the pyrite phases.

⁵⁷Fe Mössbauer spectra of virgin coals exhibit phase assemblages comparable to those observed by x-ray diffraction (XRD), e.g. pyrite and (Ca,Fe)CO₃, even though the presence of pyrite is less definitive in the XRD data.

Introduction

The usefulness of ⁵⁷Fe Mössbauer spectroscopy for the analyses of iron-containing phases in coal has been clearly established and is relevant for questions ranging from coal formation to its combustion and even possible cleaning methods [1,2]. Subtle differences in the Mössbauer spectra of coals have been found to be correlated with systematic changes in the iron-containing phases present. For example, in the case of iron disulfides, the relative amounts of pyrite and marcasite is calculable in a straightforward manner based on minor changes in the quadrupole splitting parameter, ΔEQ [3].

When investigating iron disulfide phases in coal, other iron containing phases commonly present may hinder an accurate analysis. However, the treatment of whole coal samples by exposure to a mild hydrofluoric acid is capable of removing these additional phases and thereby facilitating the analysis.

Experimental

Four coal samples from South Africa have been analyzed by ^{57}Fe Mössbauer spectroscopy in a manner described previously [3]. The powdered samples, which passed a 325 mesh sieve, were prepared under acetone and mildly sedimented onto glass slides for X-ray diffraction (XRD) analysis. XRD data was collected by scanning from 6° to 66° 2θ under $\text{CuK}\alpha$ radiation. Each coal samples was ashed by heating in a muffle furnace at 475°C for 2 days to achieve constant weight.

Results and discussion

The ^{57}Fe Mössbauer spectra for virgin coals A-D are presented in Figure 1, with Mössbauer parameters given in Table 1. For coals A-D the major iron-containing phase is an iron disulfide phases such as pyrite or marcasite, although the data suggests a variety of other iron-containing phases comprising approximately 10% to 50% of the total iron present. An iron carbonate phase, such as siderite or ankerite, was commonly present.

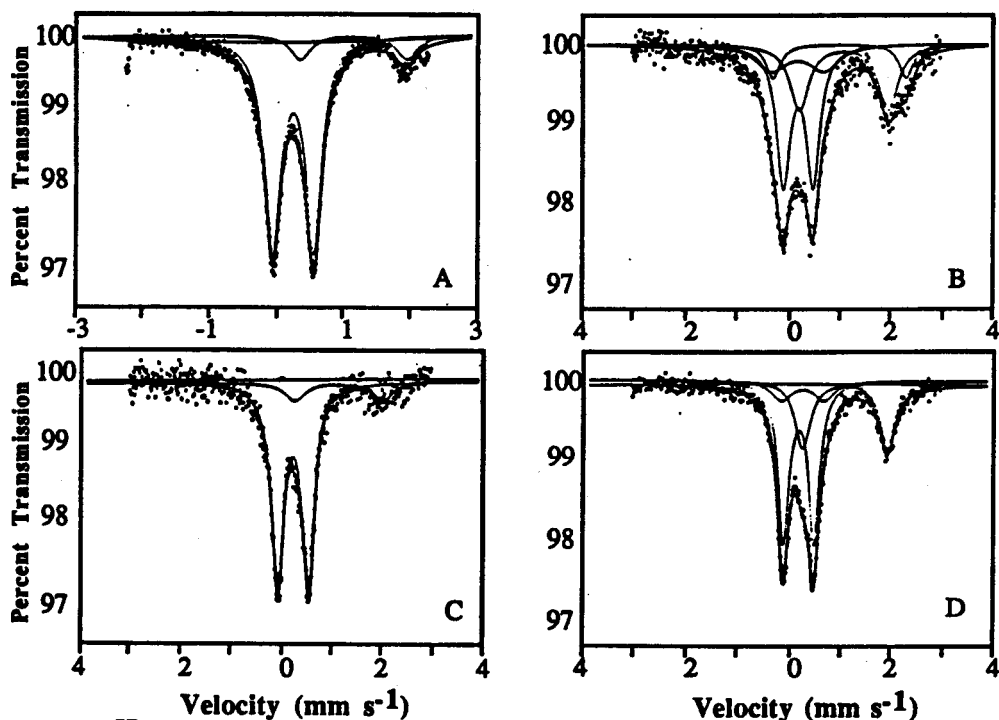


Figure 1. ^{57}Fe Mössbauer spectra for virgin coal samples A-D.

Table 1. ^{57}Fe Mössbauer parameters and phase identification for virgin coal samples.

Virgin Coal	Subspectra	Quadrupole Splitting (mm/s)	Isomer Shift (mm/s)*	Area (%)	Iron-containing Phase Identification
Coal A	I	0.62	0.30	93	pyrite
	II	1.64	1.23	7	ankerite
Coal B	I	0.60	0.31	46	pyrite
	II	1.05	0.30	19	jarosite
	III	1.79	1.23	25	siderite
	IV	2.66	1.14	10	clay (illite)
Coal C	I	0.62	0.30	90	disulfide
	II	1.79	1.26	10	siderite
Coal D	I	0.60	0.30	49	pyrite
	II	1.73	1.22	34	siderite
	III	0.81	0.33	17	clay (illite)

*Isomer shift values reported with respect to iron metal. Error in quadrupole splitting and isomer shift parameters approximately $\pm 0.03 \text{ mm s}^{-1}$.

The XRD data confirmed ankerite, $\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$, as a minor mineral phase in all four samples. Jarosite, a weathering product of pyrite, was not identified by XRD, however alunite, the Al analog of jarosite, was tentatively identified. The dominant mineral phases in all four samples were quartz and kaolinite.

To remove the iron carbonate and iron silicate phases, in addition to any other iron-containing non-iron disulfide phases, virgin coal samples were treated at 298K with hydrofluoric acid. For a given powdered coal sample, 20% hydrofluoric acid was added and the mixture stirred with a Teflon coated magnetic bar stirrer for several hours. Following the decanting of the supernatant, HF solution, the coal was washed with distilled water on filter paper and air dried. Such an experimental procedure has been shown to leave iron disulfide phases unaffected [4]. For coal samples A-D, the loss of mineral matter with HF leaching is closely correlated with the mineral matter residue following low temperature ashing (Table 2).

Representative Mössbauer spectra of coal samples following HF leaching are shown in Figure 2. The Mössbauer parameters calculated for the iron disulfide phases in coals A-D are given in table 2. The Mössbauer spectra were each fit with a single quadrupole doublet with ΔE_Q values in the range $0.619 \leq \Delta E_Q \leq 0.622 \text{ mm s}^{-1}$. These parameters differ slightly but systematically from those of pyrite for which a quadrupole splitting of 0.611 mm s^{-1} has been established. From this data it is possible to conclude that marcasite is not present at significant concentration in these treated coals and that the only iron-bearing phase present is pyrite. Further, the data suggest that the pyrite may contain a substitutional impurity such as arsenic.

It has been shown that the presence of marcasite and its concentration relative to pyrite may be determined by ^{57}Fe Mössbauer spectroscopy [3]. As the mole fraction of marcasite increases, the quadrupole splitting of the doublet arising from a pyrite and marcasite mixture decreases. Equation (1) expresses this relationship,

$$\Delta E_Q^M = 0.114 X_{\text{py}}(\text{mm s}^{-1}) + 0.500 (\text{mm s}^{-1}) \quad (1)$$

where X_{py} is the mole fraction of pyrite in a pyrite/marcasite mixture and ΔE_Q^M is the measured quadrupole splitting of the spectrum of the mixture. The quadrupole splitting values in the present investigation ($\Delta E_Q > 0.611 \text{ mm s}^{-1}$) clearly preclude the presence of significant concentrations of marcasite in any of the treated coal samples.

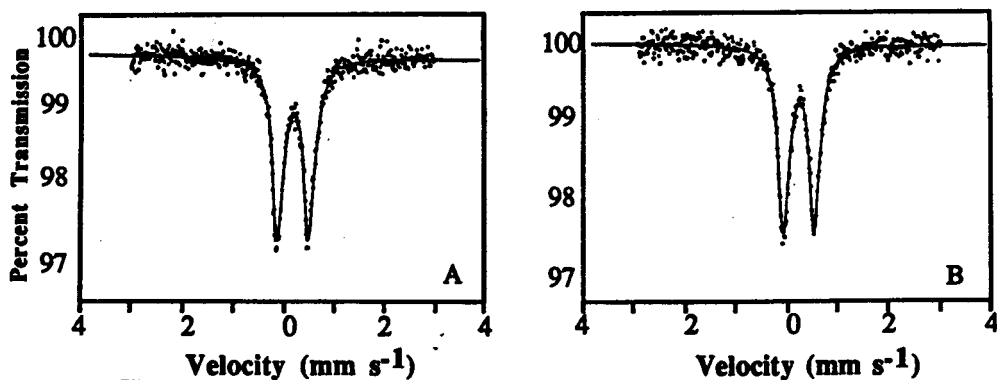


Figure 2. ^{57}Fe Mössbauer spectra for HF leached coal samples A and B.

The increased ΔE_Q values for pyrite coals A-D may be attributable to substitutional impurities such as arsenic. Consider the Mössbauer parameters for the following series of metallic chalcogenides and pnictides: FeS_2 , $\Delta E_Q=0.611 \text{ mm s}^{-1}$; FeAsS , $\Delta E_Q=1.16 \text{ mm s}^{-1}$; FeAs_2 , $\Delta E_Q=1.74 \text{ mm s}^{-1}$. The trend of increasing quadrupole splitting as arsenic content increases for $\text{FeAs}_x\text{S}_{2-x}$ suggests that a minor arsenic impurity may be present in coals A-D which results in the systematic increase of quadrupole splitting values for these samples. Alternatively, the substitution of another pnictide such as antimony (FeSb_2 ; $\Delta E_Q=1.30 \text{ mm s}^{-1}$) could also lead to an increased quadrupole splitting.

In principle, the trend in the spectral parameters could be consistent with a mixture of marcasite and arsenic-rich pyrite. However, the lines would exhibit significant deviations from Lorentzian profiles and the doublet would exhibit significant asymmetries in the depth of the absorption maxima: neither of these characteristics are observed in the spectra.

Table 2. Mössbauer parameters for post HF-leached coal samples, along with percent weight loss from HF leaching and percent residue following ashing.

Coal Sample	Quadrupole Splitting (mm/s)	Isomer Shift (mm/s)	Weight loss with HF leaching	Ash Residue
Coal A	0.619	0.308	25%	26%
Coal B	0.621	0.309	30%	34%
Coal C	0.622	0.306	23%	27%
Coal D	0.619	0.309	18%	24%

Any conclusion regarding minor substituents in these coal samples based on their influence on the Mössbauer parameters of pyrite would have been much more tentative were it not for the hydrofluoric acid treatment described in this investigation. The overlapping of the pyrite quadrupole doublet with quadrupole doublets arising from other iron-bearing phases in the virgin coal samples makes the unambiguous determination of the pyrite Mössbauer parameters significantly more difficult. The usefulness of the acid treatment noted in this investigation is clearly evident, particularly so when a thorough analysis of the iron disulfide phases in coal is required.

References

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