

Mössbauer study of the inorganic sulfur removal from coals

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Abstract Mössbauer Spectroscopy (MS) was applied to study the occurrence and behavior of the iron-sulfur-containing minerals in coal and coal fractions obtained by different separation methods: hydrocyclonic, flotation and chemical removal process. Samples of one high sulfur coal from Guachinte mine (Valle, Colombia) and three low sulfur coals from the El Salitre zone (Paipa-Boyacá, Colombia) were analyzed. MS evidenced only the presence of pyrite in Esmeralda and Las Casitas coals, while it identified pyrite and siderite on Cerezo coal. MS and SEM- EDX confirm the inorganic sulfur removal on Guachinte coal submitted to hydrocyclonic removal process. MS of the precipitated coal fraction from Las Casitas mine obtained by flotation in water showed the presence of ferrous sulfate because of coal-weathering process. Treatment with hot diluted HNO₃ equal to 27 acid on raw coal sample from Las Casitas mine showed that almost all of the pyrite in raw coal was removed.

Keywords Coal · Inorganic sulfur removal · Mössbauer spectroscopy

1 Introduction

Coal is mainly used for power worldwide. It is estimated that about 41 % of global electricity is generated from coal. In Colombia are the major reserves of coal from Latin American, 6.7 Gton dispersed in different zones in the country.

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As it is known, sulfur in coal occurs in two principal forms [1, 2]: organic sulfur and inorganic sulfur. The inorganic sulfur includes pyritic-sulfur (monosulfides and disulfides) and sulfate-sulfur (in combination with Ca or Fe). Free sulfur is present only sporadically. The presence and amounts of these sulfur forms vary considerably in coals from diverse origin. ASTM standard test method for forms of sulfur in coal, D 2492, is very laborious. Sulfate sulfur is extracted from the analysis sample with dilute hydrochloric acid (HCl). The sulfate sulfur in the extract is determined gravimetrically. Sulfates are soluble in HCl acid, but pyritic and organic sulfur are not. Pyritic sulfur is calculated from an analysis of the iron content of a nitric acid (HNO₃) solution. The iron is determined by atomic absorption techniques. The organic sulfur is then determined by the difference between the inorganic sulfur (sulfate + pyritic sulfur) and the total sulfur in the original material. The major objection to this standard method is the fact that an error in any one step of the procedure can affect the values determined in other portions of the method.

In our work, ⁵⁷Fe transmission Mössbauer Spectroscopy (MS) was applied in order to study the occurrence and behavior of the iron-sulfur-containing minerals in coal and coal fractions obtained by different separation methods: hydrocyclonic, flotation and chemical removal processes. MS is applied specifically to obtain a better characterization of the iron-sulfur-containing minerals of the analyzed samples.

The iron-sulfur-containing minerals play an important role in all coal-conversion processes (beneficiation, carbonization, combustion, gasification, liquefaction and pyrolysis): severe pollution caused by sulfur in coal during its combustion is considered to be responsible for acid rain, ozone layer depletion and several other harmful effects on the environment [3, 4]; previous work has indicated that pyritic-sulfur is the most important source of trace-elements such as As and Se in coal [5–7]; problems in technological performance (problems of fouling and slagging) [8, 9]; health impacts (respiratory problems of humans and animals [10, 11]; organic sulfur is chemically bound to the coal and very difficult to remove by physical methods, while inorganic sulfur is not bound chemically and could be removed to certain degrees from the raw coal. It is essential to reduce inorganic sulfur contents in particular and mineral matter contents in general from coal prior to its utilization. The study of different physical and chemical properties of the coal has contributed to various sulfur removal methods which involve a large variety of physical, chemical and biological processes [8, 12–16].

2 Experimental

Samples of beneficiated and precipitated coal obtained in a hydrocyclone separation unit with grain size between 600 to 1000 μm from Guachinte mine (Valle, Colombia) were selected for SEM-EDX (Scanning Electron Microscopy—Energy Dispersive X-ray analysis) studies. SEM-EDX analysis was carried out using a JEOL 8900R system. Mössbauer and XRD characterization of the mineral matter of coal from Guachinte mine were reported before [17]. The mineral phases identified by XRD were kaolinite, quartz, pyrite, gypsum, dolomite and calcite. MS confirm the presence of pyrite and kaolinite, besides evidence the additional presence of jarosite which was not detected by XRD due their low amount. The Guachinte mine coals are used

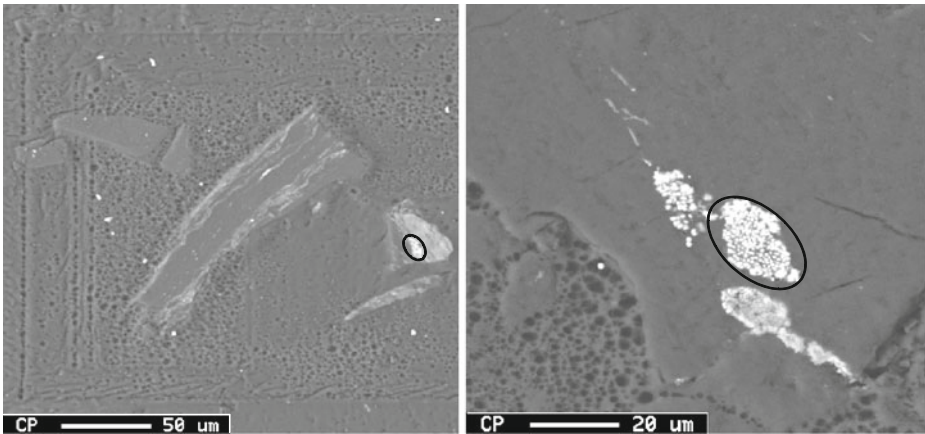


Fig. 1 SEM images of a general view of beneficiated coal product (*left side*) and precipitated coal product (*right side*) by hydrocyclonic separation process. In the *circles* were identified clusters of grains of pyrite

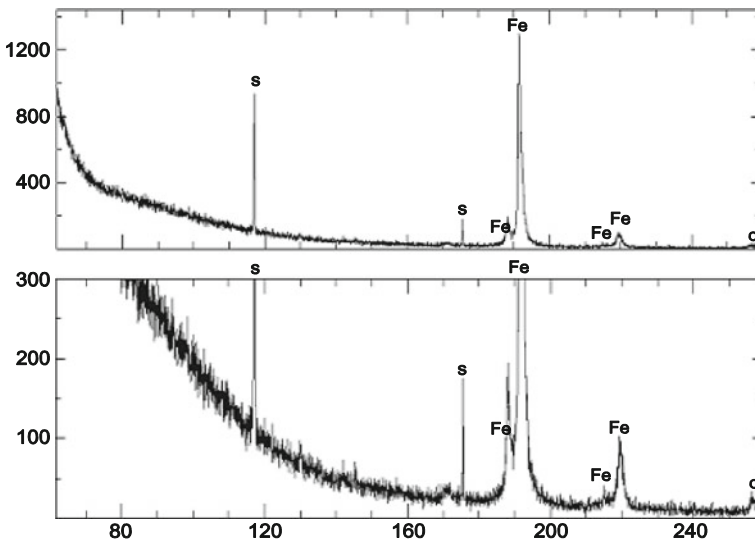
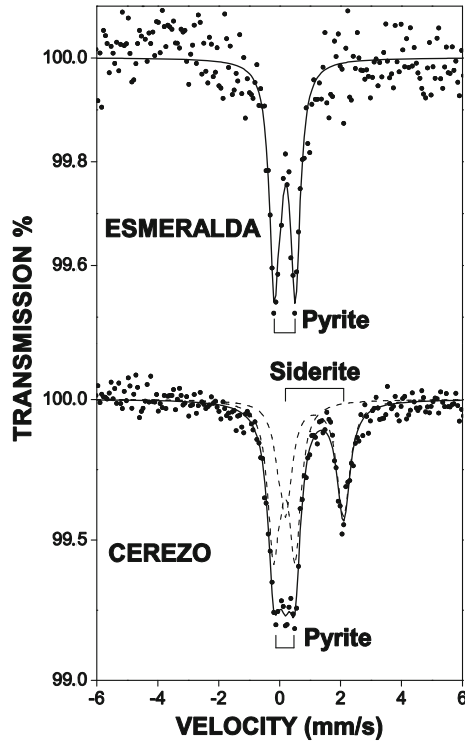


Fig. 2 EDX spectra associated with the grains of pyrite (FeS_2) identified in the Fig. 1

for combustion in the power generation plants for sugar, paper and cement local industry.

Run of mine coal samples from Cerezo, Esmeralda and Las Casitas mines located in El Salitre zone (Paipa-Boyacá, Colombia) were prepared according to ASTM standard procedure, D 2013 (pulverized to pass No. 60 (250 μm) sieve). These coals are used in the thermal power station TERMOPAIPA located to 40 Km of our laboratory.

Fig. 3 Mössbauer spectra of the Cerezo and Esmeralda coals, El Salitre zone, Paipa, Boyacá, Colombia



Proximate analysis, total sulfur and ash contents were determined according to ASTM standard procedures. Sulfur removal (*SR*) or ash removal (*ASHR*) are defined as:

$$SR \text{ (or } ASHR) = \frac{X_o - X}{X_o} \times 100 \%,$$

where X_o is equal to initial value of sulfur or ash, and X is equal to corresponding residual value after removal process.

The flotation method in water was used for to study the removal of iron-sulfur-containing minerals on coal from Las Casitas mine with grain size 250 μm . Raw coal from Las Casitas mine was desulfurized and demineralized by treatment with hot dilute nitric acid. The experimental procedure was carried out with 100 g coal and 400 ml dilute nitric acid. The mixture in a glass beaker was heated in a stove for 8 min. The coal residues were filtered and dried in air.

For Mössbauer analysis the grain size of samples used was 250 μm . Mössbauer spectra of raw coal or coal fractions were recorded at room temperature using a conventional spectrometer with a $^{57}\text{Co/Rh}$ source and calibration with respect to iron metal. The spectra were fitted using the VARFIT and MOSSFIT programs.

Table 1 Mössbauer parameters of phases identified of the coals from El Salitre zone

Sample	IS [mm · s ⁻¹]	QS [mm · s ⁻¹]	H (KOe)	Phase
Cerezo	0.28	0.64	0	Pyrite
	1.23	1.90	0	Siderite
Esmeralda	0.30	0.62	0	Pyrite
Las Casitas	0.27	0.50	0	Pyrite

Table 2 Ash and total sulfur analysis of coals from El Salitre zone

Sample	Ash [wt. %]	Total sulfur [wt. %]
Cerezo	19.83	0.76
Esmeralda	14.25	0.69
Las Casitas	12.63	1.10

Table 3 Proximate analysis of coal Las Casitas mine

Analysis	ASTM standard	Air-dried	Dry
Moisture [wt. %]	D 7582	10.61	
Volatile matter [wt. %]	D 7582	40.26	45.04
Ash [wt. %]	D 7582	11.29	12.63
Fixed Carbon [wt. %]	D 3172	37.84	42.33
Calorific Power [BTU/Lb]	D 5865	10952	12252
Total sulfur [wt. %]	D 4239	0.98	1.10

3 Results and discussion

SEM-EDX analysis confirms the presence of the pyrite phase in the samples of the hydrocyclonic removal process applied to the Guachinte coal. Figure 1 show SEM images of a general view of beneficiated coal product (left side) and precipitated coal product (right side). In the circles were identified clusters of grains of pyrite. An increase in the pyrite content is evident in the precipitated coal fraction. These images have revealed the presence of pyrite in the form of clusters of framboidal particles. These images are representative of a common way which pyrite crystals occur in coal. It is well known that the pyrite in the coal is present in different forms [18–21]. Figure 2 shows EDX spectra associated with the grains of pyrite identified in the Fig. 1.

Figure 3 shows the Mössbauer spectra of raw coal samples from Cerezo and Esmeralda mines. The Esmeralda coal produced the simplest spectrum where the only identified phase was pyrite. In the spectrum of the Cerezo coal one can note the presence of pyrite and siderite. Table 1 shows Mössbauer parameters of the identified phases for coals from El Salitre zone. The identified phases in Cerezo and Esmeralda coals by Non-Rietveld XRD single analysis were kaolinite, quartz and pyrite. Table 2 shows ash and total sulfur analysis of coals from El Salitre zone.

Proximate analysis of the Las Casitas coal is presented in Table 3. This is a high-volatile B Bituminous coal in according to ASTM standard procedure, D388. Figure 4 (Top) shows Mossbauer spectrum of Las Casitas coal, this spectrum was fitted with one only doublet corresponding to pyrite.

Fig. 4 (Top) Mössbauer spectrum of the Las Casitas coal. (Middle) Mössbauer spectrum of the precipitated coal fraction in water. (Bottom) Collapsed spectrum of the coal treated with hot dilute nitric acid

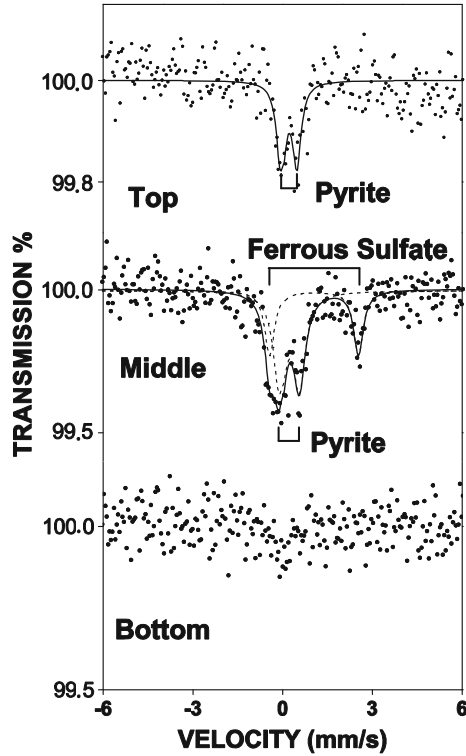


Table 4 Mössbauer parameters of the precipitated coal fraction in water

Sample	IS [mm · s ⁻¹]	QS [mm · s ⁻¹]	H (KOe)	Phase
Precipitated	0.27	0.63	0	Pyrite
	1.10	2.92	0	Ferrous sulfate

Coal from Las Casitas mine

Habitually, the coal is pretreated before use. When a coal is pulverized, its mineral components may be liberated from the coal particles, producing as pure mineral particles. The mineral grains in pulverized coal can be named included or excluded. Included mineral grains are associated with or contained within a carbonaceous coal particle. Excluded mineral grains do not have any carbonaceous material associated with them. The flotation process is a method for desulfurizing fine coal and is based on the assumption that coal is easily floatable whereas pyrite is not. In practice, included pyrite particles often float with the coal.

Figure 4 (Middle) shows Mössbauer spectrum of the precipitated coal fraction sample from flotation process in water. This spectra was fitted with a doublet corresponding to pyrite and a doublet corresponding to ferrous sulfate (FeSO_4 , $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). For revision of the values earlier reported in the literature was chosen FeSO_4 (with $\text{QS} = 2.92$ mm/s) [22]. The ferrous

Table 5 Total sulfur and ash analysis of the coal fractions from Las Casitas mine

ASTM standard	Sample	Analysis dry	
		Total sulfur [wt. %]	Ash [wt. %]
D 4239 – D 7582	Floated	1.15	11.78
	Precipitated	1.26	13.22
	Extract	0.50	7.15

Table 6 Comparative of the reductions in values of total sulfur (SR) and ash (ASHR)

Sample	Removal method	SR [%]	ASHR [%]	Resultant effect
Guachinte	Hydrocyclonic	23.8	73.8	High removal
Cerezo	Hydrocyclonic	–	65.9	High removal
Esmeralda	Hydrocyclonic	–	21.5	High removal
Las Casitas	Flotation	No change	6.73	Coal-weathering
Las Casitas	HNO ₃ Acid	54.5	43.4	Desulphurization and demineralization

sulfate is found as a result of weathering and oxidation of pyrite. The iron-bearing minerals in general are particularly sensitive to weathering [23]. Table 4 shows the Mössbauer parameters of the precipitated coal fraction from Las Casitas mine. Table 5 shows total sulfur and ash analysis of floated and precipitated coal fractions and of the extract product treatment with hot dilute nitric acid on the original coal sample.

The MS evidenced the presence of only pyrite in Las Casitas coal. Then our aim was remove this pyrite. Results of experimental procedure carried out over a sample of Las Casitas coal treated with hot dilute nitric acid indicate that the coal was desulfurized and demineralized by removal of the original pyrite. In Fig. 4 (Bottom) shows the collapsed spectrum of coal sample treated with hot dilute nitric acid. The reductions in values of total sulfur and ash of all the removal processes are compared in Table 6.

4 Conclusions

There exist differences in occurrence and contents of minerals for coals from diverse origin. SEM-EDX allows one to confirm the presence of mineral phases and elemental compositions in coals and by-products. There is evidence of an increment of the pyrite content in precipitated coal fraction obtained by hydrocyclonic removal process.

The only iron-sulfur phase identified by Mössbauer spectroscopy on samples of coal from Salitre zone (Paipa, Boyacá-Colombia) was pyrite. The pyrite was not removed in the flotation process. Besides, it promotes the presence of sulfate sulfur by coal-weathering process. It can be concluded that the coal from Las Casitas mine treated with hot dilute nitric acid was desulfurized and demineralized. MS plays an important role in the characterization of the iron-sulfur-containing minerals present in coals.

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