

## Mössbauer study of the effect of gamma irradiation on the removal of pyrite from Colombian coals

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**Abstract.** The removal of sulfur from the coals is necessary before using it. It is due to the environmental and technological problems that it causes. In this work, the results of the study by Mössbauer spectroscopy of the gamma-irradiation effect on the pyrite in three Colombian coals are analyzed. They were exposed to different gamma-irradiation doses using a <sup>60</sup>Co source.

### 1. Introduction

The forms of sulfur in coals are elemental, organic and inorganic. Elemental sulfur is present only sporadically in trace amounts. The organic sulfur is chemically bound to the carbon matrix and it is complex to remove it by physical methods. Inorganically, it can be found as i) sulfide and ii) sulfate sulfur. In the first case it can be combined with iron in different ways; being pyrite (FeS<sub>2</sub>) the most common. In the second case, it can be found as iron sulfate (e.g., Jarosite (XFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, ferrous sulfate FeSO<sub>4</sub>, Rozenite (FeSO<sub>4</sub>•4H<sub>2</sub>O), etc.) or calcium sulfate.

When studying coals, <sup>57</sup>Fe Mössbauer spectroscopy is widely accepted because it is a non-destructive technique with high sensitivity; useful for studying materials containing a mixture of iron compounds. However, the fitting of the spectra is not straightforward: in coal samples it is usual to have several Fe minerals that can show overlapping in the Mössbauer spectra. Also, the hyperfine parameter values can be affected by crystallinity, particle size and substitution. Therefore, these aspects should be taken into account when the Mossbauer spectra are fitted. A way to deal with these limitations is to obtain Mössbauer spectra at different temperatures.

The removal of iron-sulfur minerals from coals is necessary before their combustion because these minerals cause sulfur oxides SO<sub>x</sub> (i.e., SO<sub>2</sub>, SO<sub>3</sub>) associated with environmental and health problems. In addition, the relative amount of pyrite usually influences the formation of agglomeration, abrasion, corrosion, tackiness.

In preliminary works, methods used to remove Fe-S minerals have been studied. These methods consist of a treatment with hot nitric acid; and two physical methods, using flotation and hydrocyclone separation [1]. Some studies about a novel method for desulfurization of Indian and Egyptian coals using gamma irradiation have been published [2-4].

In this work, the purpose is to investigate the effect of gamma irradiation on the pyrite present in three Colombian coals by Mössbauer spectroscopy.



## 2. Experimental Procedure

Representative coal samples obtained from the mines Guachinte (Valle state), Las casitas and La Cañada (El Zalitre Zone, Boyacá state) were dried, milled (particle size 250  $\mu\text{m}$ ) and hermetically stored. Characterization studies of the samples from Guachinte and Las casitas, such as their chemical analysis and Mössbauer results were published elsewhere [1,5]. Information about ash values, total sulfur content, volatile matter and calorific value of the sample from La Cañada has been reported in this work according to the ASTM rule [6].

**Table 1.** Mössbauer results of the samples measured at 90 K. The quadrupole shifts ( $2\varepsilon_Q$ ), quadrupole splittings ( $\Delta E_Q$ ) and isomer shifts ( $\delta$ ) are given in mm/s, the hyperfine fields ( $H_M$ ) are in kOe and the areas (S) are given in % (\* *Fixed parameter*)

Sample	Phase	$H_M$	$2\varepsilon_Q/\Delta E_Q$	$\delta$	S
GUA284	Goethite	482.5	-0.25	0.47	32
	Pyrite		0.62	0.38	25
	Jarosite		1.2	0.46	28
	Kaolinite		2.73	1.41	15
GUA1800	Goethite	481.3	-0.23	0.49	31
	Pyrite		0.62	0.38	24
	Jarosite		1.2	0.46	30
	Kaolinite		2.72	1.41	15
CAS284	Pyrite		0.63	0.30*	100
CAS1800	Pyrite		0.63*	0.30*	4
	Iron Sulfate		1.78	0.87	96
CAN284	Pyrite		0.60*	0.36	75
	Jarosite		0.93	0.63	18
	Iron Sulfate		2.37	1.54	7
CAN1800	Pyrite		0.60*	0.28	1
	Jarosite		0.97	0.79	45
	Iron Sulfate		2.09	0.9	54

Homogeneous samples with approx. 20 g of mass of three coals were simultaneously irradiated with gamma photons from a  $^{60}\text{Co}$  source. The used source is part of a Theratron 780, Model C146, which had an activity of 7143 Ci to November 2008. At the time of irradiation of the samples, May 20th, 2013, the equipment presented a reference rate of 118.48 cGy  $\text{min}^{-1}$  at 80 cm distance from the source. This equipment is located at the clinic for cancer of the city of Tunja (Boyacá).

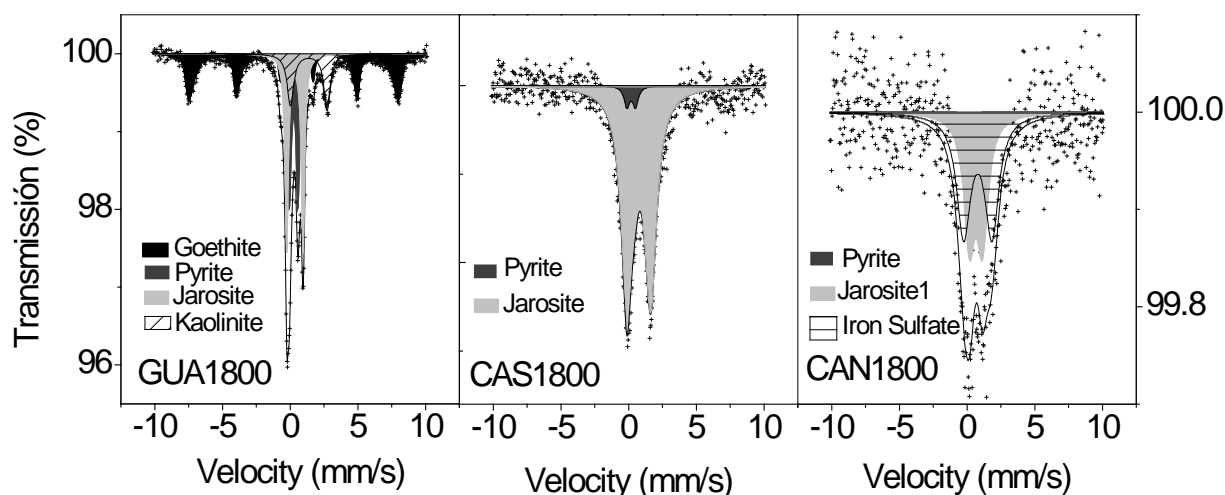
The samples were placed at a distance of 40 cm from the source (minimum distance allowed by the equipment). Irradiation dose of 10 min was carried out to complete 380 min corresponding to 1800 Gy, the maximum dose given to the samples. Subsamples of the three coals, approx. 1000 mg, were extracted after being irradiated with 284 Gy; and a second set of approx. 1000 mg was taken out after receiving 1800 Gy. The samples were named GUAX (Guachinte mine), CASX (Las casitas mine) and CANX (La Cañada mine), being X the radiation dose.

For the Mössbauer analysis, the standard absorbers were prepared containing 100 mg of sample. Mössbauer measurements in transmission mode were performed at 90 K by using a conventional spectrometer with constant acceleration and using a source of  $^{57}\text{Co}/\text{Rh}$ . The velocity scale was

regularly calibrated acquiring a spectrum of standard  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The values given for the isomeric shift are referenced with respect to the  $\alpha$ -Fe at room temperature. The measurements were made on speed ranges between -10 and 10 mm/s. DIST3E program was used for the analysis of the Mössbauer spectra, which is based on hyperfine parameter distributions. More details about this program can be found in [7]. The mineral phase identification was made by comparing the Mossbauer parameter values that were obtained with the values reported in the literature for coals and also for pure compounds [8-9].

### 3. Results and Discussion

All the Mössbauer spectra obtained from the Guachinte mine samples were fitted with three doublets and a sextet, corresponding to the phases Pyrite, Jarosite, Kaolinite and Goethite, respectively (see Figure 1 left). Regarding the spectrum of the natural sample [5], it shows that there is a reduction of Pyrite in favor of the Jarosite, Kaolinite sulfates and the Goethite oxyhydroxide for all the radiation doses. The presence of Goethite is due to the high oxidizing conditions. The hyperfine parameters of the samples GUA284 and GUA1800 are listed in Table 1.



**Figure 1.** Mössbauer spectra obtained after gamma irradiation of 1800 Gy from coal samples.

The Mössbauer spectrum having the lowest (not shown here) irradiation dose (284 Gy) for the Las casitas sample, exhibit a unique phase associated to the mineral Pyrite (see Table 1). It is in agreement with the spectrum for the natural coal [1], meaning that applying the lowest irradiation dose; there is no reduction in the content of Pyrite for these samples.

The spectrum obtained for the highest gamma irradiation for the CAS sample shows a significant reduction of pyrite, accompanied by a formation of Jarosite as shown in Figure 1 (center). The prominent doublet corresponding to Jarosite has high values of the isomer shift and quadrupole splitting (Table 1). This can be explained by the presence in the structure of high spin Fe<sup>3+</sup> [4].

Figure 1 (right) shows the typical spectrum obtained by Mössbauer spectroscopy for all the irradiation doses from the La Cañada mine samples. The spectra were fitted with three doublets, corresponding to the Pyrite, Jarosite and Iron Sulfate. The hyperfine parameters listed in Table 1 show a reduced pyrite accompanied by an increase of the Jarosite and Iron sulfate. Table 1 presents the values of the Mössbauer parameters corresponding to the samples from the La Canada mine.

Table 2 lists the results of the chemical analysis of the coals from the La Cañada mine according to the standard procedure ASTM D388. As shown in the table, it corresponds to the coal with lower ash content.

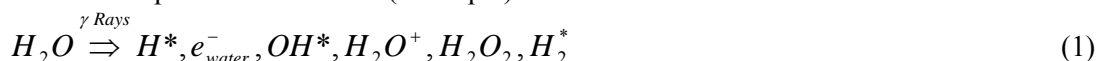
**Table 2.** Chemical analysis of the coal from the La Cañada mine.

Analysis	ASTM standard	Air-dried
Moisture [wt. %]		0.45
Volatile matter [wt. %]	D7582	52.02
Ash [wt. %]	D7582	3.64
Fixed Carbon [wt. %]	D3172	44.12
Calorific Power [cal/g]	D5865	6845.03
Total sulfur [wt. %]	D4239	0.71

Taking into account the differences between the Mössbauer results for each coal and comparing the chemical properties of them (see results in this paper, references [1,5] and Table 2), the effect of the irradiation is strongly correlated with the chemical properties of the coals such as mineral matter, ash, and sulfur content.

In the energy range of 100 keV -10 MeV the radiation absorption is primarily due to Compton effect. In this case, approximately 99% of gamma photons emitted from the Co-60 are of 1.17 MeV, which interact with the sulfur. Sulfur electronic configuration allows energy transfer with the photons achieving the desired effect.

The effect of the Gamma irradiation on the sulfur-iron minerals can be explained with the gamma radiolysis of the water present in the coals (see Eq. 1).



Due to the presence of oxygen other products also can be formed. These radiolitic products generate an oxidizing atmosphere. It is expected that if the oxidation increases, the content of sulfides decrease in favor of ferrous and ferric sulfates and possibly a formation of oxyhydroxides could appear.

#### 4. Conclusions

Coal samples of three different Colombian mines, with high and low values of pyritic sulfur content, have been irradiated with a high gamma radiation dose with the aim of achieving the desulfurization of them. The Mössbauer results show that with the given dose, the desired effect is achieved. However, it is not fully removed. These results suggest that the high costs and processes that are necessary to obtain radioactive sources and the locative physical changes for handling them would make impractical the use of this method for thermoelectric companies that use coal.

#### 5. References

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