REMOVAL OF PYRITE IN COLOMBIAN COALS BY USING GAMMA RADIATION

REMOCIÓN DE PIRITA EN CARBONES COLOMBIANOS USANDO RADIACIÓN GAMMA

J. A. Mejía[*], F. Reyes Caballero[**], C. A. Palacio[*], E. De Grave[***], H. Olaya Dávila[**], S. A. Martínez Ovalle[**]

ABSTRACT

Mejía J. A., F. Reyes Caballero, C. A. Palacio, E. De Grave, H. Olaya Dávila, S. A. Martínez Ovalle: Removal of pyrite in colombian coals by using gamma radiation. Rev. Acad. Colomb. Cienc., 37 (1): 75-78, 2013. ISSN 0370-3908.

In this contribution the results of a study by Mössbauer spectroscopy of the gamma-irradiation effect on the pyrite phase present in two Colombian coals are reported. The coals were exposed to different gamma-irradiation doses using a ^{60}Co source. It is known that the removal of sulfur from coal is necessary before using it as an energy source. This requirement results from the various environmental issues that sulfur-bearing species cause upon burning.

Key words: Pyrite, coals, gamma radiation.

RESUMEN

En esta contribución se reportan los resultados de un estudio Mössbauer acerca del efecto de la radiación gamma sobre la pirita que está presente en dos carbones colombianos. Los carbones fueron expuestos a diferentes dosis de radiación gamma proveniente de una fuente de ^{60}Co. Se sabe que es necesaria la remoción del sulfuro del carbón para ser usado como fuente de energía. Este requerimiento viene de los diferentes problemas ambientales que causan los componentes que contienen sulfuro cuando son sometidos a altas temperaturas..

Palabras clave: Pirita, carbones, radiación gamma.

---

[*] Universidad Antonio Nariño-sede Tunja, Tunja, Colombia. E-mail: juliethmejia@uan.edu.co

[**] Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia.

[***] Ghent University, Ghent, Belgium

1. Introduction

Sulfur is present in coals in different forms, which are either elemental, organic or inorganic. In the case of the elemental sulfur S, it is present only occasionally in trace amounts. In the case of the organic sulfur, it is complicated to remove it from the coal by physical methods because it is chemically bound to the carbon matrix. Finally, in the inorganic case, S can be found as sulfide or as sulfate. In the first situation sulfur forms pyrite (FeS_2) as the most common component after it combines with iron in different ways. In the second situation, various iron sulfates e.g., Rozenite ($FeSO_4 \bullet 4H_2O$), ferrous sulfate ($FeSO_4$), Jarosite ($XFe_3(SO_4)_2(OH)_6$, etc. can be found,, or S can also be found as calcium sulfate.

When studying coal materials, the ^{57}Fe Mössbauer spectroscopy is a tool which is broadly applied. It is a non-destructive technique, with a high sensitivity, that gives information of the spectral parameters that are involved with the chemical state of the iron (Fe) and to its local chemical environment. By itself, the technique is very convenient for studying materials that contain combinations of iron compounds. However, in the Mössbauer spectra (MS) the presence of different Fe minerals in the coal samples strongly overlap, which makes the fitting very complicated. Also, the particle size, crystallinity, and substitution of certain particular phase may affect the hyperfine parameters of that individual Fe phase. Hence, when the MS are fitted, these aspects should be taken into account. These limitations can be handled by collecting MS at different (low) temperatures.

The removal of iron-sulfur minerals from coals prior to their combustion is necessary because these minerals cause sulfur oxides SOx (i.e., SO_2, SO_3) to be released and these are associated with environmental and health problems. In addition, the relative amount of pyrite usually influences the formation of agglomeration, corrosion, abrasion, tackiness. In preliminary works, methods used to remove Fe-S minerals have been examined. One method consists of a treatment with hot nitric acid, whilst two other physical methods use flotation and hydrocyclone separation (**Reyes & Martinez** 2013). Some studies concerning desulfurization of Indian and Egyptian coals using gamma irradiation have been reported (**Ram *et al.*** 1997, **Tripathi *et al.*** 2011, **Ahmed *et al.*** 2011).

In this work, the effect of gamma irradiation on the pyrite phase present in two Colombian coals is studied by means of Mössbauer spectroscopy.

2. Experimental Procedure

Coal samples were obtained from the mines Guachinte (Valle state) and Las Casitas (El Zalitre Zone, Boyacá state). The chemical analyses and Mössbauer results at room temperature of the samples were published elsewhere (**Reyes *et al*** 2003, ***Reyes & Martinez*** 2013).

20 g of the coal samples were placed at a distance of 40 cm from a ^{60}Co source which is part of a Theratron 780, Model C146. At the time of the irradiation, the equipment presented a reference rate of 118.48 cGy min^{-1} at 80 cm distance from the source. This equipment is located at the clinic for cancer of the city of Tunja (Boyacá). Subsamples of the two 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) and CASX (Las casitas mine), X being the radiation dose.

Mössbauer spectra (MS) in transmission mode were obtained from the samples at ~90 K, using a conventional spectrometer with constant acceleration drive and with a source of ^{57}Co/Rh. The velocity scale was regularly calibrated by acquiring a spectrum of standard α-Fe_2O_3. DIST3E program was used for the analysis of the MS, which is based on hyperfine parameter distributions (**Vandenberghe *et al.*** 1994). The mineral phase identification was made by comparing the adjusted Mossbauer parameter values with the values reported in the literature for coals and also for pure compounds (**Huffman & Huggins** 1978, **Gracia et al.** 1999).

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

Sample	Phase	H_M	$2\varepsilon_Q/\Delta E_Q$	δ*	S
GUA284	Goethite	482.5	-0.25	0.47	32
	Pyrite		0.62	0.38	25
	Jarosite		1.20	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		1.20	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

* The values for the isomeric shift are referenced with respect to α-Fe at room temperature.
**Fixed parameter

3. Results and Discussion

Three doublets and a sextet were used to fit the MS from the Guachinte mine samples, corresponding to the phases pyrite, jarosite, kaolinite and goethite, respectively (see Figure 1(a)). Compared to the spectrum of the non-irradiated natural sample (**Reyes *et al*** 2003), it shows that there is a reduction of pyrite in favor of jarosite, kaolinite sulfates and goethite for all radiation doses. The presence of goethite is due to the highly oxidizing conditions. The hyperfine parameters of the samples GUA284 and GUA1800 are listed in Table 1.

The resulting Mössbauer spectrum of the Las Casitas sample irradiated with 284 Gy (not shown here) is in agreement with the spectrum for the natural coal (***Reyes & Martinez*** 2013); which exhibits a unique phase associated to the mineral pyrite (see Table 1). It means that applying such low dose does not reduce the content of pyrite for this coal species. In contrast, the spectrum obtained for the CAS sample after the highest irradiation dose shows a significant reduction of the pyrite phase, accompanied by a major contribution of jarosite (see Figure 1(b)). 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^{3+} (***Ahmed*** **et al.** 2011).

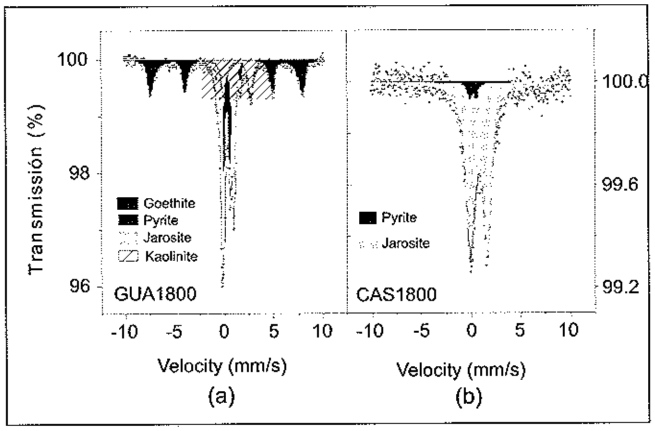

Figure 1. Mössbauer spectra at ~90 K obtained for the samples from (a) Guachinte and (b) The casitas after gamma irradiation of 1800 Gy.

Taking into account the differences between the Mössbauer results for each coal and comparing the chemical properties of them (**Reyes *et al*** 2003, ***Reyes & Martinez*** 2013), the effect of the irradiation is strongly correlated with the chemical features 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 the gamma photons emitted from the ^{60}Co exhibit an energy of 1.17 MeV, and this radiation interacts with the sulfur. The S electronic configuration allows energy transfer from the photons to the S species, thus achieving the desired effect on the Fe-S minerals. This effect can be explained by the gamma radiolysis of the water present in the coals:

$$H_2O \overset{\gamma\,Rays}{\Rightarrow} H^*, e^-_{water}, OH^*, H_2O^+, H_2O_2, H_2^* \qquad (1)$$

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 decreases in favor of ferrous and ferric sulfates and possibly a formation of oxyhydroxides takes place.

4. Conclusions

A high gamma radiation dose has been applied to coal samples obtained from two different Colombian mines. The samples, initially with high and low values of pyritic sulfur content, have been irradiated with the purpose of reaching their desulfurization. The Mössbauer results indicate that with the given radiation dose, the desired effect is only partly achieved, the sulfides being not fully removed. These finding suggests that the high costs and processes to obtain radioactive sources, and the physical changes, in locative terms, which are necessary for handling them would make the application of this method of desulfurization non-practical for thermoelectric companies that use coal for their fuel.

5. Bibliography

Ahmed, M. A., Mousa, M. A. A., Amami, S. M., Etmimi, K. M., & Ellid, M. S. (2011). Gamma Irradiation of Pyrite in Egyptian Coal as Studied by Means of Mössbauer Spectroscopy at Room Temperature. *Source Part A* 34 227-234.

ASTM, 1991. Annual Book of ASTM Standards.

Gracia, M., Marco, J. F., & Gancedo, J. R. 1999. Uses and perspectives of Mössbauer spectroscopic studies of iron minerals in coal. *Hyperfine Interact* **122**(1-2) 97-114

Huffman, G. P., & Huggins, F. E. 1978. Mossbauer studies of coal and coke: quantitative phase identification and direct determination of pyritic and iron sulphide sulphur content. *Fuel*, *57*(10), 592-604.

Ram, L. C., Tripathi, P. S. M., Jha, S. K., Sharma, K. P., Singh, G., & Mishra, S. P. 1997. γ-irradiation of coal and lignite: effect on extractability. *Fuel Process Technol.* **53** 1-14.

Reyes, F., Alcázar, G. P., Barraza, J. M., Bohórquez, A., Tabares, J. A., & Speziali, N. L. 2003. Mössbauer and XRD characterization of the mineral matter of coal from the Guachinte mine in Colombia. *Hyperfine Interact.* **148**(1-4) 39-46

Reyes F and Martinez Ovalle S A 2013 *Hyperfine Interact.*Mössbauer study of the inorganic sulfur removal from coals 10.1007/s10751-013-0874-x.

Tripathi, P. S. M., Mishra, K. K., Roy, R. R. P., & Tewari, D. N. 2001. γ-Radiolytic desulphurisation of some high-sulphur Indian coals catalytically accelerated by MnO_2 *Fuel Process Technol.* **70** 77-96

Vandenberghe, R. E., De Grave, E., & De Bakker, P. M. A. 1994. On the methodology of the analysis of Mössbauer spectra..*Hyperfine Interact.* **83** 29-49