Mössbauer characterization of feed coal, ash and fly ash from a thermal power plant

F. Reyes Caballero · S. A. Martínez Ovalle ·
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Abstract The aim of this work was apply ^{57}Fe Transmission Mössbauer Spectroscopy at room temperature in order to study the occurrence of iron-containing mineral phases in: 1) feed coal; 2) coal ash, obtained in different stages of the ASTM D3174 standard method; and 3) fly ash, produced when coal is burned in the TERMOPAIPA IV thermal power plant localized in Boyacá, Colombia. According to obtained results, we can conclude the occurrence of pyrite and jarosite in the feed coal; Fe^{2+} and Fe^{3+} crystalline paramagnetic phases, superparamagnetic hematite and hematite in coal ash; Fe^{2+} and Fe^{3+} noncrystalline and crystalline phases, magnetite and hematite in fly ash. Precisely, for a basic understanding, this work discusses some the possible transformations that take place during coal combustion.

Keywords Feed coal · Coal ash · Fly ash · Mössbauer spectroscopy

1 Introduction

The need to produce more electric power in a coal-fired power station leads to an increased coal consumption causing consequently an increased combustion waste generation. Considerable fly ash amounts are generated as a result of the high coal consumption, especially with the increases in the coal consumption with high mineral matter contents.

The fly ash is an industrial by-product which is recognized as an environmental pollutant. At the present time, the TERMOPAIPA IV thermal power plant localized in Boyacá, Colombia produces 200 ton of fly ash per each 1500 ton of burned coal, and all the fly ash produced are marketed as a raw material for the local cement industry. However, other

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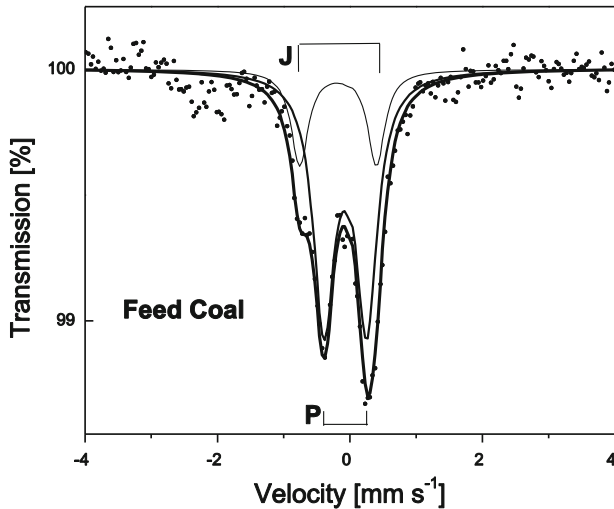e-mail: s.agustin.martinez@uptc.edu.co

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Fig. 1 Mössbauer spectrum of the feed coal; P: pyrite, J: jarosite

applications must be investigated to recycle in case of a bigger fly ash production. Fly ash contains alkaline oxides and plant nutrients that are useful in agriculture [1, 2]. Synthetic zeolites can be obtained for hydrothermal treatment of fly ash [1–8].

The nature of the produced fly ash by combustion is related with the mineral content of the feed coal and operating conditions in the thermal power plant. In order to have a basic understanding of possible transformations that occurred at iron-containing mineral phases during coal combustion in the TERMOPAIPA IV thermal power plant, the purpose of the present work was examine the occurrence of iron-bearing mineral phases in: 1) feed coal; 2) coal ash, obtained in different stages of the ASTM D3174 standard method; and 3) fly ash, produced when the coal is burned in the thermal power plant.

2 Experimental

The coal prepared as feed for the TERMOPAIPA IV power plant represents a blend of coals from several different mines with specific criteria of calorific value and ash content (particularly, ash with a wt% <23 %), among which are include coals from the Cerezo, Esmeralda and Las Casitas mines located in El Salitre zone (Paipa-Boyaca, Colombia), whose results of chemical and Mössbauer characterization were reported recently [9].

Various feed coal samples were heated in oxidation conditions of according to stages of the ASTM D3174 standard ashing method. This method correspond to the determination by weighing of the inorganic residue as ash after burning the coal under rigidly controlled conditions of sample weight, temperature, time, atmosphere and equipment specifications. An analysis sample of approximately 1 g is introduced in a cold muffle furnace and heated gradually so that the temperature reaches 500 °C in 1 h and 750 °C in 2 h. Continue the ashing at 750 °C for two additional hours.

A representative fly ash sample was collected from one bank of hoppers located below of the electrostatic precipitation system. The representative composition from the fly ash was

Table 1 Mössbauer parameters of identified phases for feed coal, standard ash test and fly ash

Sample	IS [±0.01 mm •s⁻¹]	QS [±0.01 mm •s⁻¹]	H [±1 KOe]	$\Gamma_{1/2}$ [±0.01 mm •s⁻¹]	A [±1 %]	Phase
Feed Coal	0.30	0.61	0	0.19	76	Pyrite
	0.41	1.12	0	0.16	24	Jarosite
Ash 750-4h	0.37	0.17	514	0.17	69	Hematite
	0.34	0.82	0	0.31	8	Superparamagnetic Hematite
	0.27	1.72	0	0.91	23	Fe^{3+}
Ash750-2h	0.37	0.18	514	0.16	66	Hematite
	0.35	0.71	0	0.17	5	Superparamagnetic Hematite
	0.34	1.66	0	0.71	29	Fe^{3+}
Ash500	0.37	0.18	510	0.25	41	Hematite
	0.35	0.73	0	0.31	44	Superparamagnetic Hematite
	0.94	2.29	0	0.30	15	Fe^{2+}
Fly ash	0.28	0.0	495	0.58	15	Magnetite
	0.50	0.0	456	0.38	9	Magnetite
	0.41	-0.19	514	0.38	3	Hematite
	0.91	2.62	0	0.40	34	Fe^{2+}
	0.36	0.89	0	0.23	11	Fe^{3+}
	0.61	1.04	0	0.30	17	Fe^{3+}
	0.97	1.36	0	0.42	8	Fe^{2+}
	0.98	1.40	0	0.18	3	Fe^{2+}

IS= Isomer Shift, QS= Quadrupole Splitting, H= Magnetic Hyperfine Field,

$\Gamma_{1/2}$ = Half Line Width, A= Absorption Area

determined using a wavelength-dispersive X-ray fluorescence spectrometer. In addition, X-ray powder diffraction data from the fly ash were determined using a diffractometer with Cu-Kα radiation. The scan was obtained with a step size of 0.013° in 2θ and a counting time of 33 s per step.

The Mössbauer data were taken at room temperature using a conventional spectrometer with a ^{57}Co/Rh source and calibration with respect to iron metal. The Mössbauer spectra were fitted using the MOSSFIT program.

3 Results and discussion

Figure 1 shows the Mössbauer spectrum of the feed coal sample. This spectrum was fitted with two doublets and the obtained Mössbauer parameters (see Table 1) are typical of the pyrite (FeS_2) and jarosite $XFe(SO_4)_2(OH)_6$ with X = K+ or Na+ or H_3O^+ or NH_4^+) minerals. The pyrite has a common occurrence in Colombian coals. It is accepted that the presence of jarosite is result of the effect of natural weathering of the pyrite [10–14].
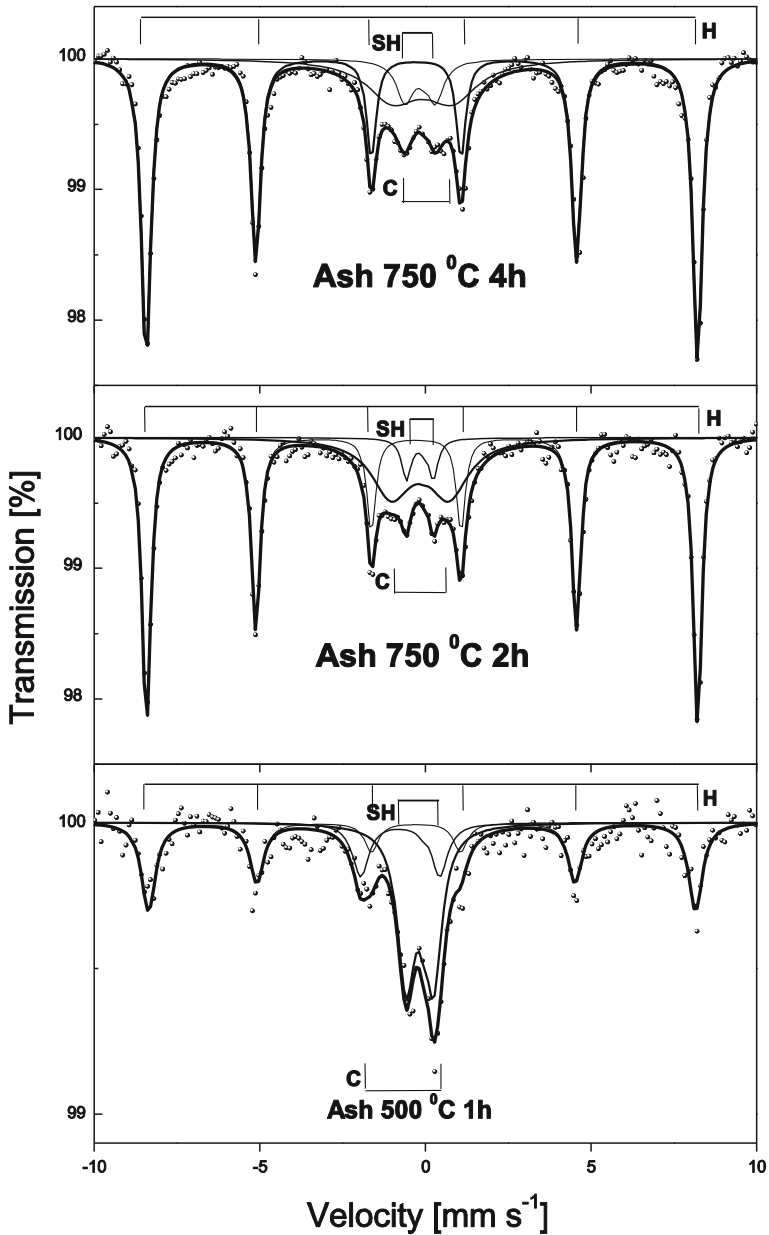
Fig. 2 Mössbauer spectra of the standard ash test; H: hematite, SH: superparamagnetic hematite, C: clay

It is expected that the iron-bearing minerals during heating undergo a series of physical and chemical changes. The ASTM D3174 standard method was useful to obtain results of the coal heating until temperatures 500 and 750 °C with different heating times. Figure 2 (Bottom) shows the Mössbauer spectrum of the Ash 500 °C 1 h sample. Figure 2 (Middle) presents the Mössbauer spectrum of the Ash 750 °C 2 h sample. Figure 2 (Top) is the

Table 2 Representative composition from the fly ash

Element	[wt %]
SiO_2	62.11
Al_2O_3	25.66
Fe_2O_3	3.70
K_2O	1.87
TiO_2	1.11
CaO	0.53
MgO	0.50
P_2O_5	0.50
Na_2O	0.29
BaO	0.11
SrO	0.07
V_2O_5	0.06
ZnO	0.03
Ignition loss	3.44

representative Mössbauer spectrum of the Ash 750 °C 4h sample, final product from the standard ashing process of feed coal.

These spectra were fitted with one sextet and two doublets. In Table 1, the obtained Mössbauer parameters for the identified phases are listed. An important change during heating of coal in oxidation conditions is the conversion of iron sulfide and sulfate to iron oxide and sulfur dioxide. Therefore, the sextet and a first doublet were attributed to the oxidation of the pyrite and jarosite. The sextet corresponds to hematite (Fe_2O_3). The doublet has typical quadrupole splitting of superparamagnetic hematite [10, 14]. It is known the oxidation of pyrite and jarosite to ferric hydroxysulphate ($Fe(OH)SO_4 \bullet 2H_2O$) and of ferric hydroxysulphate to ferric oxysulphate ($Fe(OH)SO_4$) or superparamagnetic hematite. The hydroxysulphate is considerate the precursor of oxysulphate and hematite. Since that the hydroxysulphate have a particle size of 4 – 6 nm is possible that very small superparamagnetic hematite particles undergo sintering to form larger superparamegnetic hematite particles with the Mössbauer values assigned in the Table 1. It is evident that the transformations of pyrite and jarosite were 100 %. As can be seen the amount of hematite was increased with the temperature and time of ashing. The absorption area of the sextet associated to hematite was increased relative to the total area. Therefore, with the increase heat, it can be stated that the final oxidation product must be hematite.

The second doublet for the Ash 500°C 1h sample was attributed to the reasonable presence of clay with iron in Fe^{2+} state. It is well known the dominance of Fe^{2+} state in clays present in coals [10, 11, 13]. However, this phase not was detected in the analyzed feed coal sample due to its sporadic presence. In the Ash 750 °C 2h and Ash 750 °C 4h samples, due to the heating, can be noted the iron conversion of Fe^{2+} state to Fe^{3+} state. The changes in the isomer shift and quadrupole splitting may be attributed to the well-known loss of water of constitution in clay minerals (to temperatures of 300 - 600 °C) and to the collapse of structure (to temperatures >600 °C) consequences of the heating process. It is known a strong correlation between the percentages of Fe^{3+} content in the paramagnetic phases (possibly, glass or poorly crystalline with large line width) in ash with the percentage of Fe^{2+} in clays presents in their parent coals [13].
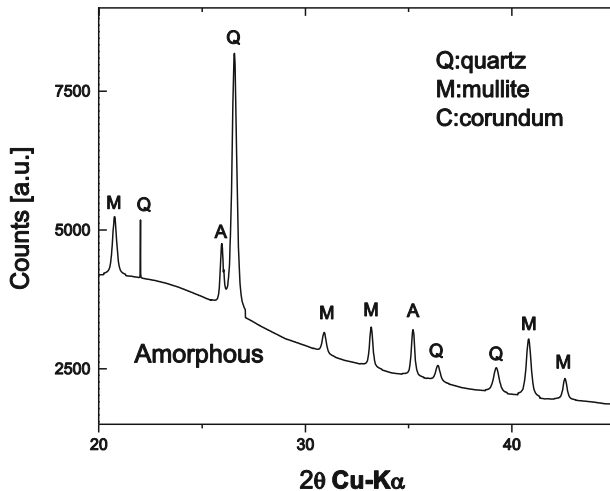
Fig. 3 X-ray powder diffraction pattern of the fly ash; Q: quartz, M: mullite; C: corundum

Results of the compositional analysis from the representative fly ash sample are listed in Table 2. This fly ash is characterized chemically by that SiO_2, Al_2O_3 and Fe_2O_3 make up around 90 %. They have minor much amounts of, K, Ti, Ca, Mg, P, Na, Ba, Sr, V, and Zn. XRD pattern of the fly ash, shown in Fig. 3, indicates the presence of the crystalline phases: quartz, mullite and corundum. The broad hump in the pattern indicates the presence of a significant (amorphous) glassy content. Results of Rietveld quantification indicate an amorphous content of 59 %.

The combustion in the TERMOPAIPA IV thermal power plant reaches temperatures considerably higher than 750 °C. The pulverized coal to very fine size ($\sim$50 μm) is burnt. In the process occurs the oxidation of carbon and hydrocarbons to carbon dioxide and water (efficiencies over 98 %), with release of heat. Because of the very small particle size, the interior of a particle is heated very rapidly as it enters the combustion chamber, where flame temperature of 1500 °C are common, and as a result any volatile matter is quickly release (included inorganic volatile material and oxides of sulphur and nitrogen). Is important be noted that when a coal is pulverized can be liberated relatively pure mineral particles.

In the process of formation of the fly ash occur a complex combination of physical and chemical transformations, which depend of combustion conditions and the association, size and composition of the inorganic constituents that form the ash. In the flame these inorganic species are transformed into gases, liquids and solids. Physical transformations that may be occurring during the combustion are [13, 15–18]: 1) coalescence of mineral grains during char combustion (fusion among some components); 2) evaporation and condensation; 3) formation of cenospheres; and 4) fragmentation de minerals. Besides, the fate of each inorganic constituent in the flame and during gas cooling depends on at least two factors: 1) the volatility of the component; and 2) their associations (organic and/or mineral).

Figure 4 shows the Mössbauer spectrum of the representative fly ash sample. This spectrum was fitted with three sextets and five doublets. The obtained Mössbauer parameters are listed in Table 1. Although exist a large number of reported results in the literature [19, 20], because of the complex process and characteristics of the final product that occur in the fly ash formation that were mentioned above, a completely reliable and total identification of
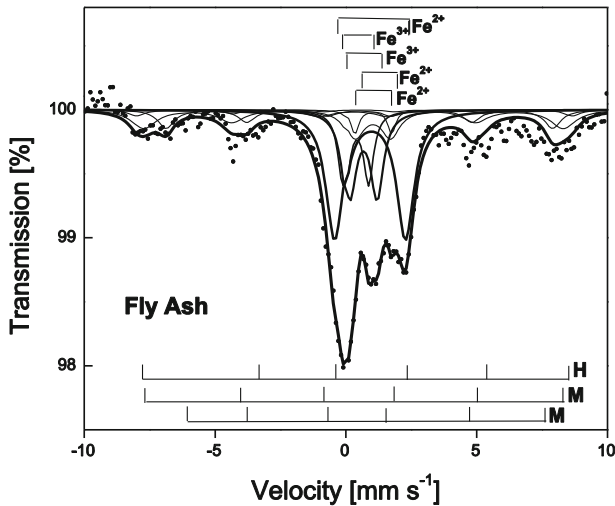
Fig. 4 Mössbauer spectrum of the fly ash; M: magnetite, H: hematite

the present phases not appear possible only with the information obtained from Mössbauer data. However, it is presented the following discussion with respect to the obtained results.

The sextets may be assigned to the magnetic phases: magnetite (Fe_3O_4) and hematite (Fe_2O_3), in agreement with reported results in the literature [12, 13]. These phases were not clearly noted in XRD pattern due their low amounts (See Fig. 3). It is evident that the occurrence of hematite and magnetite were due to the transformation of pyrite and jarosite present in the feed coal. The five doublets may be associated to Fe^{2+} and Fe^{3+} noncrystalline and crystalline paramagnetic phases. The Mössbauer and XRD results suggest: 1) Fe^{2+} phase as an original clay residue; 2) Fe^{2+} and Fe^{3+} phases as mullite or curundum formed by fusion among pyrite, jarosite, quartz and clays; 3) presence of pyrrhotite; 4) presence of wustite; 5) amorphous phases given the significant glassy content in fly ash; or 6) poorly crystalline clay mineral.

4 Conclusions

According to the obtained results we can conclude the occurrence of pyrite and jarosite in the feed coal; hematite, superparamagnetic hematite, and Fe^{2+} and Fe^{3+} paramagnetic phases in coal ash; Fe^{2+} and Fe^{3+} noncrystalline and crystalline phases, hematite and magnetite in fly ash. The pyrite is the precursor of the hematite and magnetite. In the coal combustion several different reactions take place among the components causing a strange mixture of noncrystalline and crystalline phases. This implies that for a completely reliable and total identification of the present phases, we should include other experimental methods and techniques: separation methods; crystallo-optical studies and SEM-EDX analysis.

Undoubtedly, the Mössbauer spectroscopy is one of the recommended experimental techniques for the investigation of the fly ash, given that in this wide spectrum of difficulties, it provides information useful on the qualitative and semiquantitative occurrences of finely dispersed iron-bearing minerals and amorphous phases, detection of oxidation levels of the present iron-bearing phases, and Fe^{2+}/Fe^{3+} ratios.

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