

TECHNOLOGICAL, ENVIRONMENTAL AND ECONOMIC IMPACT, OF THE MINERAL MATTER PRESENTED IN COAL

IMPACTO TECNOLÓGICO, AMBIENTAL Y ECONÓMICO DE LA MATERIA MINERAL PRESENTE EN EL CARBÓN

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ABSTRACT

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The analysis of the mineral matter contributes meaningfully to define the quality of coal. In this work we present the results of identification and quantification of mineral phases presented in samples of natural coal, and coal fractions beneficiated with concentration fractions of mineral matter, obtained by different separation methods using Rietveld-based X-ray diffraction (Rietveld-based XRD), ^{57}Fe transmission Mössbauer spectroscopy (MS) and scanning electron microscopy with energy dispersive X-Ray (SEM_EDX) analysis, which allows to identify the potential for removal of minerals. Furthermore, it is possible to explore the relationship between the ash obtained, the melting point, the calorific value and the relative proportions of the individual minerals in the samples studied. Similarly, using the information obtained, we evaluate the technological, environmental and economic impacts associated with mineral matter.

Key words: Coal quality, Mineral identification and quantification.

RESUMEN

El análisis de la materia mineral contribuye significativamente a definir la calidad del carbón. El propósito del artículo es presentar resultados de identificación y cuantificación, de las fases minerales presentes en el carbón y fracciones de carbón obtenidas por diferentes métodos de separación, usando Análisis Rietveld de patrones de difracción de rayos X, espectroscopia Mössbauer de transmisión ^{57}Fe y microscopia electrónica de barrido con análisis de energía dispersiva de rayos X. Además, fue identificado el potencial de remoción de minerales, y fue explorada las relaciones entre la ceniza obtenida, el valor calorífico y las proporciones relativas de los minerales

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individuales en las muestras estudiadas. Usando la información obtenida, se evalúan los impactos tecnológicos, ambientales y económicos asociados con la materia mineral.

Palabras clave: Calidad del carbón, Identificación y cuantificación de la materia mineral.

1. Introduction

Coal is the main and the most abundant in terms of reserves and geological resources of sedimentary fossil solid fuels: coal (<50 wt. % Ash), organic shales (50-90 wt. % Ash) and peat (Alpern and Lemos de Sousa, 2002). Coal is mostly used fuel for generating electricity in the world and current estimates indicate that 41% of global electricity is generated from its use (WCA, 2013). Several clean technologies (CCTs: Clean Coal Technologies) for the extraction, preparation and use of coal more efficient and environmentally acceptable are in used. Colombia has one of the most important reserves and resources in terms of quantity and variety of coal qualities with respect to Central and South America, from annually produce 5 to 10 Mt in the decade 1980-85 Mt in 2012 (Mt = Million tons).

Coal is a sedimentary rock, organic in nature, porous, complex, heterogeneous and stratified, formed from the fossilized remains of plants with inorganic elements incorporated. Inorganic elements are usually incorporated into the coal referred to as the "mineral matter," and contains three types of components: fluid matter (moisture and gas-liquid inclusions) through the pores of the coal, such as dissolved salts and other inorganic substances; elements inorganic associated with the organic compounds of the coal maceral (metal-organic complexes) and discrete crystalline inorganic particles (in the form of crystals, granules and aggregates) or non-crystalline (amorphous), representing true mineral components (Tascón and Vassilev, 2000).

Coal quality is defined as the coal properties and characteristics that affect its use (Finkelman, 1995; Finkelman and Pierce, 2002). Particularly, the information on the relative amount of the mineral phases, size, shape and composition of the minerals, the knowledge of the concentration and distribution of the elements between the organic and inorganic components, and washability potential or removal of an item during the benefit, contribute significantly to defining the quality of coal, due to: 1) Its influence on technological performance. In combustion processes the mineral matter is a source of unwanted agglomeration, abrasion, corrosion, inert material processing, tack, and pollution by gaseous emissions, liquid and solid, of volatile ashes, acid or alkaline solutions, toxic elements and potentially toxic compounds (Clemens *et al.*, 2000; Vassilev *et al.*, 2001). 2) Its environmental impact and human health. Most of the trace elements

presented in natural coals are associated with mineral matter. The sulfides and sulfates contain various heavy metals (such as Pb, As and Ag) and its high sulfur content are a major source of environmental damage and human health, when coal is burned without previous cleaning procedures (Finkelman and Gross, 1999).

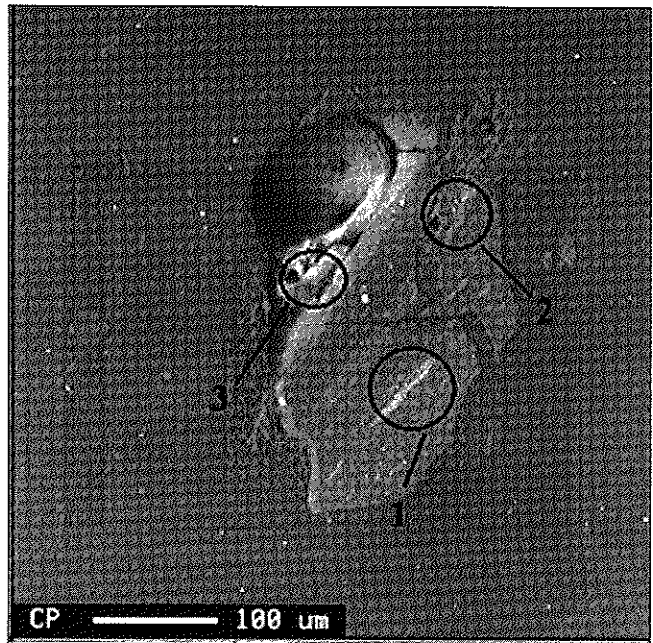


Figure 1. Electron micrograph of a fraction of beneficiated coal.

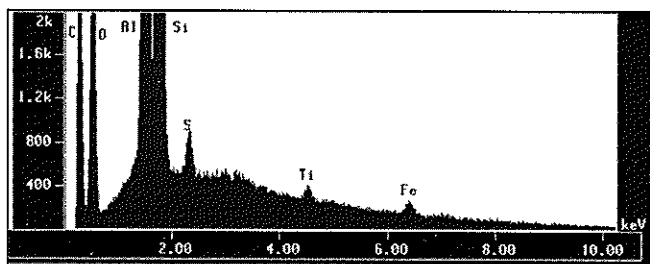


Figure 2. Analysis of X-ray energy dispersive.

3) Political and economic significance. Consumers, who currently define trading conditions, require coals meet strict specifications. 4) The use of residues of its benefit and processing. Globally, a fairly large number of projects are directed to find uses and recovery processes of waste byproducts of profit and coal processing (ACAA, 2013). 5) Its geoche-

mical significance. Mineral matter provides important information on the conditions of sedimentation and geologic history of the sequences containing the robes of a coal mine (Ward, 2002).

The purpose of our work is basically to apply analysis Rietveld of X-ray patterns diffraction, ^{57}Fe Mossbauer spectroscopy of transmission and scanning electron microscopy with energy dispersive analysis of X-rays, to identify and quantify the mineral matter presented in Colombian coals. In this paper it is reported the identification of the potential for removal of minerals. Furthermore, it is examined the relationship between the calorific value and relative proportions of individual minerals. Similarly, using the information obtained are evaluated technological, environmental and economic impacts associated with mineral matter.

2. Experimental

In the study we have analyzed representative samples, air-dried and homogenized, from original material taken from Mine head with different ash contents of mines from Boyacá, Cundinamarca, Valle and Cauca. Different subsets have been subjected to various and different removal processes of mineral matter (physical: for example, floating, separation hidrociclónica and gamma irradiation separation, chemicals: treatment with dilute nitric acid and hot (Reyes Caballero *et al.*, 2002; Reyes Caballero and Martínez Ovalle, 2013).

All samples were reduced to a particle size of 250 μm (No. 60 mesh), for analyzes according to ASTM standards (ash determinations, total sulfur, calorific value, etc.). (ASTM, 1991).

Partial information about mineral morphology, particle size and chemical composition was obtained by electron microscopy analysis of sample and microanalysis energy dispersive fluorescence using SEM/EDX JEOL 8900R.

For the analysis by Mossbauer spectroscopy and X-ray diffraction powder, subsamples were reduced to a particle size < 74 μm (N $^{\circ}$ 270 mesh).

It was prepared Mössbauer absorber by sandwich of powders of the samples (~ 100 mg) between two paper disks in circular specimen (12 mm diameter) in order to maintain constant the thinness of the absorber. Mössbauer spectra were taken at room temperature using a conventional spectrometer in transmission mode with a constant acceleration, with a source of $^{57}\text{Co}/\text{Rh}$ and calibration with respect to metallic iron. All spectra were fitted using the programs VARFIT y MOSSFIT. The identification of mineral phases presented, was made by comparing the Mössbauer parameters values obtained with values reported in the literature (Stevens *et al.*, 1998; Gracia *et al.*, 1999).

Standard specimen were prepared with a homogeneous mixture of natural coal dust or coal fractions (~ 50 mg) with ~ 10 mg of powder of high purity Fe (99.99%) used as internal standard for the radiation diffraction analysis with Cu -K α on a Rigaku diffractometer in Bragg-Brentano geometry, 2θ - θ , with a scan speed of $0.05^\circ 2\theta / 5$ so $0.05^\circ 2\theta / 25$ s, in the range of 4° to 140° in 2θ . The mineral phase identification was performed by search-match method using a personal computer with the help of PDF-2 Database and the software Perfil (Reyes Caballero, 2005). A software had to be developed to remove very high noise (background) presented in the diffraction profile before of the refinement procedure by Rietveld (Reyes Caballero, 2005). The Rietveld refinements were performed using the software DBWS-9807 y FullProf-2001

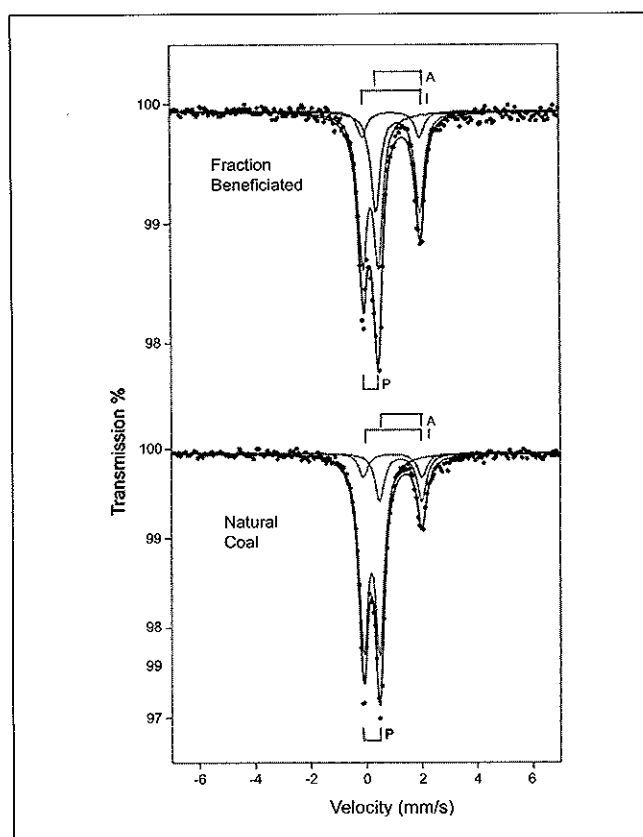


Figure 3. Mössbauer spectra of representative samples of beneficiated coal fraction (top) and natural charcoal (below), P: Pirita, A: Ankerita, I: Ilita.

3. Results and discussion

Quantification methods of mineral matter coal were initially indirect, it means, by calculating the ash content using various techniques, for example, ATSM, (2007):

$$MM=1.1CZ + 0.1AT,$$

Where CZ and AT are the values of ash and total sulfur, respectively. Today, there is the possibility of using modern methods of the mineral matter coal quantification, using electron microprobe, Mossbauer spectroscopy, analysis based on Rietveld patterns of X-ray diffraction. In Figure 1 it is showed an electron micrograph of a representative sample of a fraction of beneficiated coal. At points 1, 2 and 3 were identified clusters of pyrite grains. Figure 2 shows typical results obtained with the analysis of X-ray energy dispersive.

Table 1. Mössbauer parameters of the phases of Fe identified.

| Sample | IS ± 0.01 $\text{mm}\cdot\text{s}^{-1}$ | QS ± 0.01 $\text{mm}\cdot\text{s}^{-1}$ | RA ± 1 % | Phase |
|---------|---|---|-----------------|----------|
| Yolanda | 0.29 | 0.57 | 72 | Pirita |
| Natural | 1.35 | 1.52 | 20 | Ankerita |
| Coal | 1.02 | 2.03 | 8 | Ilita |
| Yolanda | 0.29 | 0.56 | 53 | Pirita |
| Benef. | 1.28 | 1.59 | 37 | Ankerita |
| Coal | 1.04 | 2.06 | 10 | Ilita |

Among the most important properties affecting the washability of minerals and / or elements are its modes of occurrence and their textural relationships. Elements associated with mineral phases offer the potential for removal by physical washing procedures coal. Elements associated primarily with the organic constituents will not be effectively reduced by the physical washing of the coal; on the contrary, they can be enriched in the washing of coal. Figure 3 compares the Mössbauer spectra of representative samples of beneficiated coal fraction (top) and natural coal (bottom). The identified phases correspond to Pirita, Ankerita e Ilita.. Mössbauer parameters of the phases Fe identified in the samples studied are presented in Table 1.

The spectra measured in this work allow define relative distributions of minerals and Fe concentration in the different products of the separation processes. The relative intensity of resonance Hp, peak height of Figure 3, gives the relative distribution of the phases of Fe in each sample. Relative spectral area (RA %) is considered proportional to the concentration of Fe in the sample, given the experimental conditions keeping constant spectrometer geometry and thickness of the sample. Therefore, changes in the value of the spectral area from sample to sample correspond to changes in the concentration of Fe. Mössbauer results show a Pirita remo-

val of approximately 26%, while, reflect an inherent nature of mineral matter for the phases Ankerita and Ilita.

Figure 4 shows the Rietveld Refinement for the full pattern of X- ray diffraction corresponding to a natural coal sample superimposed on the diffraction pattern of Fe, the latter used as internal standard. The mineral phases identified were Caolinita (K), Yeso (G), Dolomita (D), Calcita (C), Cuarzo (Q) y Pirita (P). The "hump" observed in X-ray diffraction profile for the region between 10° and 40° , is a characteristic pattern of X-ray diffraction corresponding to rock samples rich in organic matter such as coal. This "organic hump" is proportional to the content of organic matter in the sample (Mandile and Hutton, 1995).

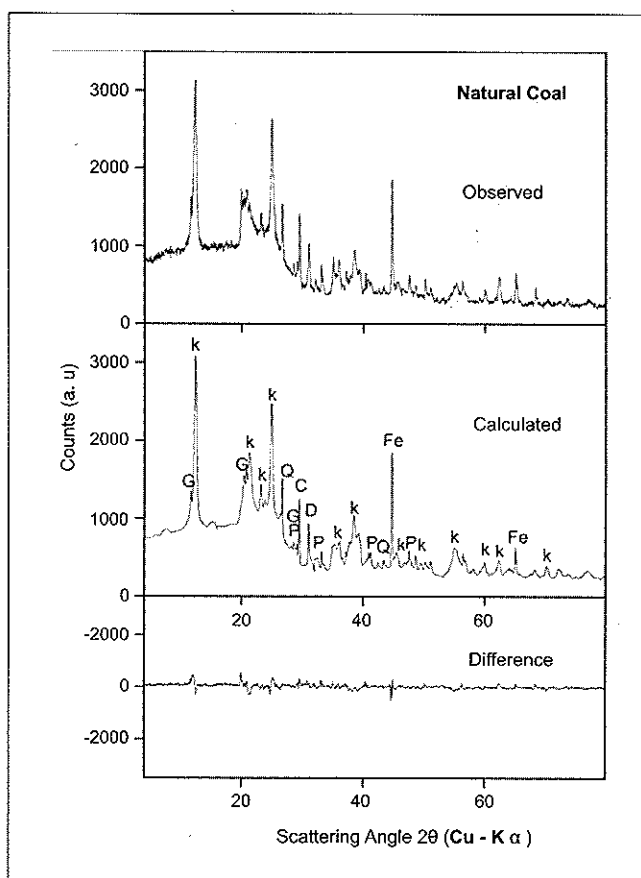


Figure 4. Rietveld Refinement of X-ray diffraction Pattern, of a natural mixture of carbon powder of Fe from high purity. K: Caolinita, G: Yeso, D: Dolomita, C: Calcita, Q: Cuarzo, P: Pirita.

The amount of ash and total sulfur determined by ASTM methods to natural coal were 25.1% and 2.2%, respectively. The concentrations of the mineral phases identified in natural coal, calculated of the Rietveld Refinement results for the full pattern of X-ray diffraction, are reported in Table 2.

Table 2. Refinement Rietveld results for the overall pattern of X-ray diffraction of a sample of natural carbon.

| Phase | Formula | Regist (PDF-ICSD) | wt. % |
|--|---|---------------------------|-------------|
| Kaolinita | H ₄ Al ₂ O ₉ Si ₂ | PDF 14-164 ICSD 63192 | 24.3 |
| Gypsum | H ₄ CaO ₆ S | PDF 33-311 ICSD 2057 | 3.1 |
| Dolomita | C ₂ CaMgO ₆ | PDF 36-426 ICSD 10404 | 1.8 |
| Calcita | CCaO ₃ | PDF 5-586 ICSD 16710 | 1.7 |
| Quartz | O ₂ Si | PDF 46-1045 ICSD 63532 | 1.5 |
| Pirita | FeS ₂ | PDF 42-1340 ICSD 43716 | 0.7 |
| Total proportion crystalline mineral material | | | 33.1 |

In Figure 5 are presented the calculated proportions of crystalline mineral matter and crystalline mineral phases for natural coal (Figure 5b) and beneficiated coal fractions (Figures 5a and 5d), and fractions of mineral matter concentration (Figure 5c and 5e). The results were obtained from the quantitative analysis based on Rietveld Refinement to the complete pattern of X-ray diffraction of the respective samples. The results show that the crystalline mineral matter represents a very important percentage of 33.1% of the total composition of natural coal. Mineral phases Caolinita y Cuarzo, are presented as foreign mineral matter in proportions of 24.3% and 1.5%, respectively. Carbonates Calcita and Dolomita are presented in the form of mineral matter inherent in proportions of 1.7% and 1.8%, respectively. Pirita and Yeso minerals are presented both as mineral matter and mineral matter odd inherent in proportions of 0.7% and 3.1%, respectively.

The mineral distribution between mineral odd matter and mineral matter inherent is associated with the amount of mineral matter that can be removed, so it is important to calculate the potential impact that can have on the cleaning processes on environmental quality, economic and technological of analyzed coal. The results show a 22% reduction in total sulfur content due to the first inorganic separation process (Figure 5b and 5a). Pyritic sulfur removal is 71%, while it is evidenced the mineral inherent matter character of the Yeso phase due to an increase of 9.5% in the pyritic sulfur content, assuming that the organic sulfur content was unchanged.

The heating value is the heat generated during the combustion of coal. In Figure 5 are presented the comparisons

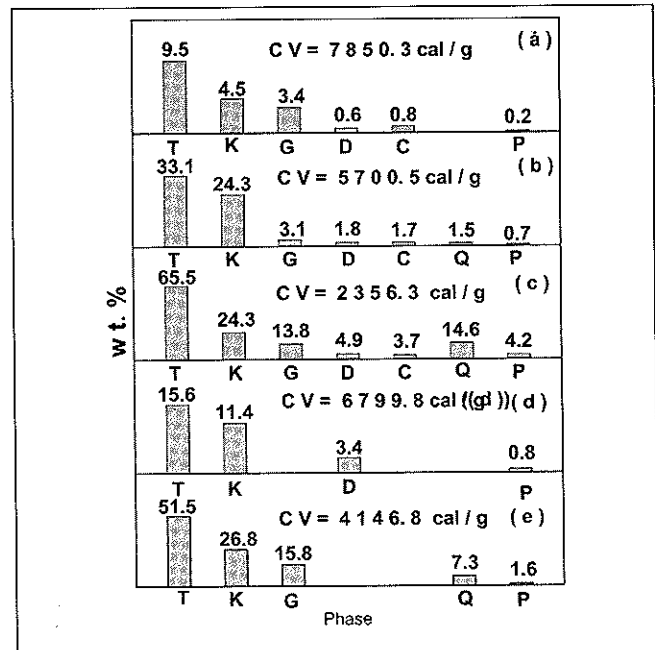


Figure 5. Calculation of ratios of total crystalline mineral matter of crystalline mineral phases presented for natural coal (b), beneficiated coal fractions (a) and (d), and fractions of coal mineral matter concentration (c) and (e). T: Total, K: Caolinita, G: Yeso, D: Dolomita, C: Calcita, Q: Cuarzo, P: Pirita.

between experimental measurements of calorific value (CV en cal·g⁻¹) and the content (wt. %) of the mineral phases for representative samples of natural coal, and beneficiated coal fractions and fractions of coal mineral matter concentration. It is interesting to notice, a decrease in the total of crystalline mineral matter of 38%, between the natural coal and the beneficiated coal fraction, leading to an increased calorific value of 71%. In coal combustion, product of the transformation during heating, Pyrite phase has a thermal effect of exothermic nature with a value of +2193 cal·g⁻¹, while the other phases have thermal effects of endothermic phase, with the largest value associated with Calcite phase - 437 cal·g⁻¹.

4. Conclusions

There are meaningful technological, environmental and economic impacts due to the content of mineral matter in the coals.

From the experience gained, it is stated that there is no universal method that provides a complete mineralogical description for coals. Each technique, X-ray diffraction, Mössbauer spectroscopy, electron microprobe, etc, has advantages and limitations.

In the combustion of coal, Pirita has an exothermic nature effect, while the other mineral phases have endothermic effects.

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