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Determination of mineral matter in Brazilian coals by thermal treatments

Vera L.V. Fallavena [a], Cristiane S. de Abreu [a], Taísi D. Inácio [a], Carla M.N. Azevedo [a], Marçal Pires [a], Lizete S. Ferret [b], Iolanda D. Fernandes [b], Rosa M. Tarazona [c]

[a] Faculty of Chemistry, Pontifical Catholic University of Rio Grande do Sul, Av. Ipiranga, 6681, CEP 90619-900 Porto Alegre, Brazil
[b] Science and Technology Foundation (CIENTEC), Rua Washington Luiz, 675, 90.010-460 Porto Alegre, Brazil
[c] Instituto Nacional del Carbón (INCAR-CSIC), C/Francisco Pintado Fe, 2633011 Oviedo, Spain

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ABSTRACT

Information about the mineral and organic fractions of coal is essential for its sustainable use. However, most analytical characterization techniques used could be affected by the presence of organic matter in the matrix. The Brazilian coal contains high levels of sulfur ash (up to 50%), being usually classified as low-rank. In this study, the mineral matter (MM) content in Brazilian coals was obtained from the ash content of samples calcined at moderate (300 °C, 400 °C and 370 °C) and low (<200 °C) temperatures with oxygen plasma (LTA). The isolate MM could be analyzed without the interference caused by organic matter. The best results for estimating the MM content from thermal treatments at moderate temperatures were obtained at 300 °C ($MTA^{C}_{300\,°C}$). Residual organic and inorganic carbon contents in the ash are recommended for a more accurate MM estimation. LTA analysis indicated MM of 45% to 62% content, similar to values obtained with $MTA^{C}_{300\,°C}$ analysis (errors < 9%). In addition, it is possible to estimate the mineral matter content with proposed empirical equations based on easily determined parameters (HTA) with mean relative errors <10%.

1. Introduction

The most important Lower Permian coal deposits in Brazil occur in the southern region of Brazil, with major coal development in the states of Rio Grande do Sul and Santa Catarina. Proven reserves are in the order of 32×10^9 tons, of which 89.2% are located in Rio Grande do Sul, 10.4% in Santa Catarina and the remainder 0.4% in the Paraná and São Paulo states [1].

Knowledge of the mineral matter (MM) in coal is important for interpreting the inorganic chemistry associated with coal formation and understanding of such phenomena as the formation of ash and slag resulting from the processing and utilization of coal [2,3]. The identification and characterization of minerals are more effective and complete if the content is concentrated or isolated from the sample. However, the ash content obtained by calcination at high temperature (HTA, high-temperature ashing) is a poor indicator of the mineral content of coal because many changes occur during combustion [4–7]. The heating of coal in air for a prolonged period at moderate temperature (350 °C–370 °C) has been used by several authors to determine the percentage of minerals in a coal sample by destroying the organic matter, improving the method sensitivity [8–11]. Although the temperature is lower than that used for the conventional determination of ash (775 ± 25 °C), the ash content is not the actual inorganic or mineral matter in coal because the ash is derived from the inorganic and organic matter of coal as well as inorganic compounds not originally present in coal [6,12]. However, the loss of volatile compounds and the incomplete attack of the matrix are potential analytical problems with this procedure [4].

According to several authors [6,9,11–22], the most efficient method for removing the organic matter of coal is concentrating mineral matter in ash using oxygen plasma at low temperature (150 °C–200 °C), known as LTA. However, there are no systematic studies about the determination of LTA in Brazilian coals. Nahuys et al. [9] were pioneers in the determination of MM content by LTA. They studied the levels of MM obtained by LTA in coal samples from the Rio Grande do Sul state (Carboniferous Basin of Candiota, Leão, Morungava, Iruí). They concluded that the ash content of coal is greater than the ash content determined at 815 °C and obtained a correction factor derived from the relationship between the ash levels obtained at low and high temperatures. However, they also found that the correction factor is variable among basins due to differences in the mineral composition of coals.

More recently, Silva et al. [23] studied the mineralogy and determined the concentration of major and trace elements in coal feed, fly ashes and bottom ashes collected from seven units of the Thermoelectric Complex Jorge Lacerda (TCJL), located in the Santa Catarina state. The ash contents obtained by LTA varied from 44.7% to 49.4%, whereas the average value for HTA (not cited in the study) of these coals is 42%. The authors noted that the coals provided by different TCJL units are similar in terms of mineral matter. The same similarity was observed for fly ashes and bottom ashes. Organically associated calcium also appears in the form of bassanite in the LTA residues.

The separation of the mineral matter of coal by LTA seems to induce less change in the MM and is therefore widely used for the identification and quantification of the minerals present in the coal samples by X-ray diffraction. However, this technique requires a long period of time to

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complete the burning of organic matter. According to Glustoker [13] and Nahuys et al. [9], the procedure may take days or even weeks. Another disadvantage of LTA is the small amount of sample that can be used due to the strong dependence of the burn rate on the particle surface area exposed to activated oxygen flow. In addition, a large number of replicates must be produced to obtain sufficient ash mass for subsequent tests.

However, if the ashes at low temperature cannot be measured directly, it is possible to obtain a reasonable value for the MM content from several proposed formulas [7,9,12,14]. These formulas permit the calculation of the MM content from various parameters determined during the coal analysis. The Parr formula (Eq. (1)) is the most frequently used in the United States and only requires the ash (HTA) and sulfur (S) contents determined in routine analysis. This correlation, in its simplest form, considers the total sulfur content in the form of pyritic sulfur and does not include the decomposition of carbonates or fixing of sulfur in ash. In addition to the limitations of and the adaptations proposed for this correlation, its advantages regarding the accuracy of MM determination were not clearly demonstrated [7,9].

$$\%\mathrm{MM} = 1.08 \times \mathrm{HTA} + 0.55 \times \mathrm{S} \qquad (1)$$

It should be noted that the experimental determination of the MM content is more strongly recommended than the use of empirical formulas applicable to coals from other basins, which often have very different characteristics.

Due to the heavy use of coal in iron making plants and power stations, detailed knowledge of the inorganic matter of this material and its behavior at high temperatures is very important. Fusibility tests of coal ash provide useful information about the behavior of this material, indicating the softening and fusion stages [24]. The ash-fusion temperature (AFT) is an important indicator of the behavior of ash in coal combustion, gasification, liquefaction or ash utilization [25].

The aim of this work was to evaluate methods for the quantification of the mineral matter in coal using different thermal treatments at moderate temperatures. Several high-ash, low-rank Brazilian coals were studied to evaluate the treatment applicability and limitations. Several techniques (XRD, SEM–EDS and elemental analysis) were employed to verify the oxidation of organic matter and possible transformations of minerals due to the ashing process. The results of the thermal treatments were correlated and compared with those obtained by LTA and empirical equation. An alternative procedure using moderate-temperature ashing followed by the unburned carbon determination on coal residue is proposed.

2. Materials and methods

2.1. Identification and preparation of the samples

Table 1 identifies all the coal samples used in this study. The raw coal samples come from different coalfields in the southern Brazil, in the states of Santa Catarina (SC) and Rio Grande do Sul (RS). Six coal samples are from the South Santa Catarina coalfield, including the Barro Branco (BBF1 and BBF2) and Bonito (BO1, BO2 and BO3) seams. The CAR sample is a washed coal, also from this coalfield, and is the first standard reference material (SRM) for Brazilian coal (Rede Metrologica-RS, Brazil). The certified parameter of the CAR sample includes the HTA content. This group of samples was used to develop the proposed thermal treatment to estimate MM. It mainly consists of samples from the South Santa Catarina coalfield due to its more intense use in thermoelectric power plants in recent decades (Barro Branco seam). Coal samples from the Bonito seam were chosen because the exploitation of this seam began more recently and it is poorly characterized. To compare the behavior, two coal samples (CRE1 and CRE2) from the Leão-Butiá coalfield in Rio Grande do Sul were also used. CRE2 and BBF2 were used to check the proposed correlation between HTA and MTA.

Table 1
Identification of the coal samples studied.

Sample ID	Coalfield	Seam	State[a]
CAR	South Santa Catarina	n.i.	SC
BBF1	South Santa Catarina	Barro Branco	SC
BBF2	South Santa Catarina	Barro Branco	SC
BO1	South Santa Catarina	Bonito	SC
BO2	South Santa Catarina	Bonito	SC
BO3	South Santa Catarina	Bonito	SC
CRE1	Leão-Butiá	M	RS
CRE2	Leão-Butiá	M	RS

n.i.: not informed.

[a] State identification: RS: Rio Grande do Sul and SC: Santa Catarina.

All raw coal samples were collected and ground to <250 μm following established procedures [26] and then stored in sealed containers in the dark under controlled temperature (20 ± 2 °C). The SRM coal sample was used as received (<250 μm).

2.2. Morphological, chemical and mineralogical characterization of the raw and treated coal samples

The proximate and ultimate analyses of the coal samples were carried out by standard methods [27–29]. An elemental analyzer (LECO TruSpec) determined the C, H, N, and S contents, and the percentage of oxygen was calculated as the remainder [30]. The main components of coal samples were evaluated by X-ray fluorescence analysis (XRF), according to ASTM D 4326:2003 standard [31], using Rigaku Dengi equipment (model RIX 3100), with rhodium radiation source. The samples, with particles smaller than 0.074 mm (sieve #200), were prepared as pellets fused at 1000 °C with $Li_2B_4O_7$ binder (the ratio of sample to binder was 1:5). In order to identify crystalline phases in the coal samples X-ray diffraction analysis (XRD) was performed using a Rigaku Dengi D-Max 2000 X-ray diffractometer with CuKα radiation at voltage 30 kV and current 15 mA. Scans were conducted from 2 to 80° at a rate of 2°θ per min. The mineral phases were identified with Jade Plus 5 software with JCPDS mineral powder diffraction database. Samples were homogenized in an agate mortar and sieved to particles smaller than 0.037 mm (sieve #400). The residual content of the carbonates, present in the ashes of the coal samples subjected to thermal treatment, was determined according to ASTM D6316-09B [32].

2.3. Thermogravimetric procedures

2.3.1. Moderate- and low-temperature ashing tests

Ashing experiments at moderate temperature (MTA), namely, 300 °C, 370 °C and 400 °C, were performed in a muffle furnace with the temperature calibrated and monitored by a type K thermocouple (chromium-alumel). Preliminary tests were performed with the CAR coal sample in which it was possible to optimize the mass of the sample and determine the type of crucible and the ideal calcinations time. Medium-sized crucibles (30 mL) containing 1.5 g of the sample produced a more effective burning than other sizes in terms of the level of ash and the residual carbon content. The burn periods were varied from 5 to 400 h, depending on the temperature and type of coal studied. To confirm the total burning of carbonaceous material, the carbon and carbonate levels in the samples were determined after the heat treatment. Possible mineralogical changes of these samples were also evaluated by XRD analysis. The determination of MM content by low-temperature ashing (LTA) using oxygen plasma (Emitech K 1050X) was performed in the Instituto Nacional del Carbón (INCAR, Oviedo, Spain) with the samples CRE1, CAR, BBF, BO1, and BO3. LTA residues were used in the characterization of minerals by XRD.