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Mineral transformations during high temperature treatment of anthracite

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ABSTRACT

SEM/EDX analysis has been applied in order to assess the mineralogical transformations occurring during high temperature treatment of several different anthracites. At 1000 °C (carbonization) loss of CO_2 from carbonates, S from sulfides and OH and/or H_2O from clays occurs, transforming these minerals to other inorganic phases such as lime, pyrrhotite, and (Na, Mg) K-aluminosilicates, among others. Heat treatment of the carbonized samples up to 1500, 2000, and 2500 °C resulted in: i) a decrease in oxygenated mineralogical phases, which are transformed to higher temperature silicates (grossite, anorthite, kushiroite, *etc.*); ii) carbide formation (SiC, TiC or Al_4C_3) by carbothermal reactions; iii) formation of alloys, especially a Pb–Sn alloy; and iv) formation of iron silicides (Fe_2Si), iron phosphides (Fe_3P), and nitrides (TiN and AlN). The new mineral phases are closely related to the mineral matter in the raw anthracite samples. Thus, samples richer in Ca–Mg phases (carbonates and phosphates) produced minerals such as monticellite, pyrope, gehlenite, grossite and kushiroite; samples richer in Al-bearing phases (boehmite and diaspore) gave rise to phases such as mullite, corundum and spinel; and Si–Al bearing phases (clay minerals) were associated with the formation of minerals such as panunzite, plagioclase and cristobalite. At the highest temperature of the process the majority of the elements vaporized, and Ti seems to be the only element in the original mineral matter that withstands treatment to 2500 °C.

1. Introduction

Coal is a heterogeneous material, composed of organic and inorganic fractions. The inorganic fraction, generally classified as "mineral matter", encompasses all the minerals and other inorganic elements, such as: i) non-mineral inorganics, which include dissolved salts and other inorganic substances present in the pore water of coal, as well as inorganic elements incorporated within coal macerals; and ii) discrete inorganic particles (crystalline or non-crystalline) representing the mineral components (Suárez-Ruiz and Crelling, 2008; Vassilev and Tascón, 2003; Ward, 2002). Non-mineral inorganic compounds are usually associated with low-rank coals (brown coals and sub-bituminous coals), and tend to disappear with increase in rank. Discrete mineral particles, however, may occur in coal of any rank and are usually the dominant component of the mineral matter in higher rank coals (Ward, 2002; Ward et al., 2001).

Minerals such as quartz, clays (kaolinite and illite), feldspars, carbonates (siderite, calcite, and dolomite) and sulfides (pyrite) are the most common crystalline phases in coals (Taylor et al., 1998; van Krevelen, 1993; Ward, 2002). However, other minerals can also be found in varying proportions including phosphates, titanium minerals, other carbonates and silicates, and bauxite minerals (Dai et al., 2008, 2010b, 2011b; Permana et al., 2010; Rao and Walsh, 1997; Suárez-Ruiz et al., 2006; Wang et al., 2011; Ward et al., 1996), as well as trace minerals such as sphalerite, galena, chalcopyrite, monazite, and others (Dai et al., 2010a, 2011a; Hower and Robertson, 2003; Kalaitzidis et al., 2010; Koukouzas et al., 2010; Swaine and Goodarzi, 1995).

During heating, these minerals undergo chemical and structural modifications (dehydration, dehydroxylation, decomposition and formation of new phases, vitrification), changing significantly the original material. Thus, coal mineral matter transforms into other minerals to various degrees depending on the temperature and other treatment conditions.

With treatment at higher temperatures, over 1000 °C, and depending on the preparation conditions, the interaction between a metallic element present in a mineral and carbon can lead to the formation of carbides (Bishop and Hendry, 1994; González et al., 2005; Mackenzie et al., 1994; Malyshev and Hab, 2003; Panda et al., 1999; Shveikin and Perelyaev, 1997; Stoll, 2003; Wang et al., 2000) which, in turn, decompose at still higher temperatures. As explained by Oberlin and Rouchy (1971), the metallic element preferentially reacts with the disordered carbon at the boundaries of the basic structural units (BSUs) to form carbides; further decomposition leads of these phases to graphitic carbon, and the size of the already-existing graphitic layers increases. Alloys and compounds may also be formed as the temperature rises (Choi et al., 1999; Kawanowa et al., 2000; Krendelsberger et al., 2007), such as those produced in the metallurgical and ceramic industries.

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Following the work of Franklin (1951), it was established that anthracite could graphitized above 2000 °C. Since then, many efforts have been made in the sense of using different anthracites as feedstocks for production of highly valuable graphitic materials (Atria et al., 2002; Blanche et al., 1995; Duber et al., 1993; González et al., 2004; Oberlin and Terriere, 1975; Pappano and Schobert, 2009; Pusz et al., 2002, 2003; Rodrigues et al., 2011a,b; Suárez-Ruiz and García, 2007). However, as mentioned above, coals are represented not only by the carbonaceous fraction, but also by mineral matter. During high temperature treatment not only does the carbonaceous fraction undergo strong physical and chemical transformations, but also the mineral fraction may also be modified. The objective of this research was thus to explore the transformations of the minerals present in different anthracites with increasing temperature during high temperature treatment (HTT), in order to evaluate their changes during graphitization. Mineral matter in the raw anthracite was characterized using quantitative X-ray diffraction (XRD) and SEM/EDX techniques, but, due to the limited amounts of material available, the identification of inorganic phases in heat treated samples was performed using only SEM/EDX evaluations. Quantitative analysis obtained from the X-ray diffractograms using Siroquant™, commercial interpretation software (Taylor, 1991; Ward and Taylor, 1996; Ward et al., 1999), based on the Rietveld methodology, has been applied successfully in the analysis of low and high temperature ashes (LTA and HTA) and coal combustion products, as demonstrated by several authors (Dai et al., 2011b; Grigore et al., 2008; Gupta et al., 2008; Kim et al., 2009; López and Ward, 2008; Mandile and Hutton, 1995; Matjie et al., 2008, 2011; Ribeiro et al., 2010; Sakurovs et al., 2007; Ward and French, 2006; Ward et al., 2001).

Siroquant allows the quantification of more than 25 different minerals in a mixture (Ward, 2002) and also permits an evaluation of the amorphous aluminosilicate phases formed by the breakdown of clays during heat treatment (Gupta et al., 2008; Matjie et al., 2008; Ward and French, 2006). A scanning electron microscope (SEM) equipped with energy-dispersive X-ray (EDX) detectors and back-scattered electron (BSE) detector allows qualitative and quantitative chemical analysis (Gupta, 2007; Huggins, 2002). This technique can be used not only in the identification of a particular mineral phase, but also in the location and measurement of chemical elements present in trace levels in the mineral and in the identification of accessory mineral phases (Dai et al., 2010a; Swaine and Goodarzi, 1995).

Knowledge of the type, amount, distribution and evolution of the mineral matter in coal provides valuable information for geological studies (origin and history of deposition of a coal seam) (Dai et al., 2008; Ward et al., 2001). For industrial purposes, the knowledge of kind of inorganic materials that may remain in the graphitized material can help to remove them, since obtaining carbon materials of high purity is one of the prerequisites in, for example, electrochemical applications (Wissler, 2006).

2. Samples and analytical procedures

2.1. Samples

Three anthracites from different geographical and geological origins, denoted PBEB, ACB, and DB, with mean random vitrinite reflectances (Rr%) of 2.62%, 5.23%, and 6.25%, respectively, were selected for this research (Rodrigues et al., 2011a). Two of the samples are from intra-continental coal basins, namely the Peñarroya–Belmez–Espiel Basin (PBEB; Spain) and the Douro Basin (DB; Portugal), and are of Carboniferous age (lower Westphalian and lower Stephanian C, respectively). Both these basins were tectonically affected by the Variscan Orogeny. However, the coalification of the anthracites from the PBEB (western part of the basin) was also conditioned by fluid circulation resulting from magmatic activity (Marques, 2002; Suárez-Ruiz et al., 2006). In the Douro Basin, the final stages of coalification were conditioned by the intrusion of granitic bodies in the southeastern part of the basin (Pinto de Jesus, 2003), but there is no evidence to suggest that fluid circulation influenced the rank of these anthracites. The third anthracite comes from the Alto Chicama Basin (ACB; Peru) of Cretaceous age (Lower Valanginian). The ACB sample is a ball coal whose formation has been related to tectonic activity promoted by the Andean Orogeny in this basin (Carrascal-Miranda and Suárez-Ruiz, 2004).

2.2. Analytical procedures

2.2.1. Heat treatment experiments

The raw anthracites were firstly carbonized at 1000 °C in a tube furnace, under nitrogen flow, at a heating rate of 2 °C/min and with a residence time of 1 h. Separate but representative samples of each carbonized anthracite were then heated to temperatures of 1500 °C, 2000 °C or 2500 °C in a graphite furnace, under argon flow, at a heating rate of 10 °C/min, and the samples were kept at the relevant maximum temperatures for 1 h. The materials obtained from these high temperature treatments were identified by a code that included the designation of the precursor anthracite (*e.g.,* DB), the letter “C” for carbonization process (*e.g.,* DBC), and then the graphitization treatment temperature, (*e.g.,* DBC/2500).

2.2.2. Mineralogical analysis

The powdered anthracite samples were subjected to low-temperature oxygen-plasma ashing using an IPC 4-chamber asher as outlined in Australian Standard 1038, Part 22 (Standards Australia, 2000) prior to XRD analysis, and the mass percentage of low-temperature ash (LTA) was also determined. The LTA samples were analyzed using a Philips PW1830 X-ray diffractometer with Cu Kα radiation and a scan range of 2–60° 2θ. Quantitative analysis of the mineral phases in each sample were obtained from the X-ray diffractograms using Siroquant™, commercial interpretation software (Taylor, 1991), based on the Rietveld XRD analysis technique.

This analysis could not be performed on the heat treated samples due to the small amounts of mineral material available.

2.2.3. SEM/EDX analysis

The raw and heat treated anthracite samples were analyzed by scanning electron microscopy with X-ray microanalysis (SEM/EDX). The SEM/EDX analyses were conducted at the Materials Centre of the University of Porto (CEMUP) using an FEI Quanta 400FEG environmental scanning electron microscope (ESEM), equipped with a EDAX Pegasus X4M energy dispersive spectroscopy (EDX). This analysis was performed in low vacuum on polished surfaces without coating the samples and back-scattered electron (BSE) images from the surface were collected. Weight and atomic percentages of the elements for each analyzed mineral particle were obtained from EDX analyses. With these results, whenever possible, stoichiometric calculations were performed in order to identify the mineralogical phases present in the samples studied.

3. Results and discussion

3.1. Mineral matter composition of the raw anthracites

Table 1 provides proximate and ultimate analysis on the samples studied, including both the raw anthracites and the different heat treated samples.

Table 2 shows the mineral percentages in the LTA of each raw anthracite sample, as determined by XRD and Siroquant. Illite is the dominant component in all three LTAs, especially that of sample DB, along in each case with minor proportions of kaolinite and chlorite. Quartz is also a significant component of the LTA isolated from the DB sample, but is present at no more than trace levels in the other LTAs studied. Bauxite minerals are present in two of the LTA samples, with boehmite being prominent in the PBEB sample and diaspore in