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Proximate and ultimate analysis correction for kaolinite-rich Chinese coals using mineral liberation analysis

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ABSTRACT

Since the ultimate analysis of the organic fraction of coal is a critical design figure for fixed-bed gasification processes, the analyses must be corrected to take into account the effect of the volatile mineral matter which can bias the analyses. In particular, the determination of water of constitution originating from clay minerals such as kaolinite remains an elaborate task. The present paper describes the application of Mineral Liberation Analysis (MLA) to estimate the content of water bearing kaolinite in a set of five samples originating from three Chinese coals (CC1 to CC3). In order to validate the MLA, one coal sample was investigated before and after density separation to assess the change in mineral matter. Results were compared to mineral content estimations from X-ray fluorescence (XRF) oxide ash analysis. In general, the MLA data can help to identify minerals better than XRF. MLA also has the advantage over XRD by detecting amorphous material, i.e. clay mineral types. The results indicate that kaolinite is the dominant clay mineral in each sample. The bias on the ultimate oxygen content (determined by difference) ranges between 1.7 and 8.9 wt% when comparing water-and-ash-free to dry-mineral-matter-free (dmmf) basis for CC2 and CC3 samples. In the case of CC1 coal, the change in the oxygen content is less than 1.2 wt% which is within experimental error for the accuracy of oxygen determination. Assuming that the organic coal fraction of the washed and unwashed CC2 samples are similar, it was concluded that the differences in dmmf ultimate analyses are greater for the MLA correction than for the XRF correction. Hence, MLA helps defining the type of mineral species present. Subsequently, SiO_2 and Al_2O_3 contents from XRF could be assigned to kaolinite and the water of constitution was estimated more precisely.

1. Introduction

1.1. Technological background

The inorganic fraction in subbituminous, bituminous coals and anthracites can often be dominated by clay minerals such as muscovite, illite, kaolinite and montmorillonite [2]. All of them can incorporate considerable amounts of water of constitution which is only released at higher temperatures than used during standard coal drying [1]. Hence, the main impact is on ultimate and proximate analyses where the water from clay crystal decomposition is added to the volatile matter fraction. Oxygen and hydrogen contents are also distorted [2], which is a particular problem because these values are essential figures used for fixed-bed gasification process design. It is therefore vital to accurately quantify the mineral-originated portion of those elements. The target of the investigation is to provide a suitable analysis of clay water which can be used for the correction of the ultimate and proximate analyses.

Many coals undergo the beneficiation process of coal washing to reduce the ash yield. Therefore, Mineral Liberation Analysis (MLA) data are often available besides standard information from proximate, ultimate, and XRF ash analyses in an industrial environment. The main objective of this study is to investigate if the available MLA data can be used to correct the proximate and ultimate analyses regarding volatile mineral matter without requiring any further analyses. Furthermore, the XRF oxide ash composition can be used to validate the accuracy of the detected minerals composition from MLA.

1.2. Impact of minerals on elemental and proximate analysis

The impact of mineral matter on the coal analysis is especially important if the mineral fraction releases gaseous compounds. The mineral carbon content can be corrected easily since CO_2 orig-

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inating from carbonates can be determined using standard analyses [3]. The same is true for sulfur originating from pyritic and sulfate mineral compounds [4]. In contrast, the water originating from hydrated clay minerals (such as kaolinite, muscovite, illite, and montmorillonite) cannot be determined easily. It has a minor impact on the hydrogen fraction but a significant impact on the oxygen fraction from elemental analysis. Furthermore, the oxygen fraction is determined by difference [5]. This implies that it not only includes the inaccuracies of the other elements (CHNS) but also the difference between mineral matter and ash. With subbituminous, bituminous coals and anthracites, the oxygen content is reported as too high. Gumz et al. [2] showed hard coals with 21.3 wt% ash on a water-free basis (wf) as having a bias of up to 4.8 wt%(wf) in the oxygen concentration due to mineral water.

In the case of Chinese coals, it has been reported that Shanxi, Hebei, Inner Mongolia and Shandong province have Carboniferous-Permian coals with clay (kaolinite strata) originating from sedimentary alteration of volcanic ash. In particular, Daqingshan coal from Inner Mongolia, as well as Taiyan coal of Tongchuan area and Datong coal area of Shanxi province are prominent for kaolinite inclusion [6]. Hence, the focus of the present investigation is placed on the impact of kaolinite. The coal ash resulting from kaolinite decomposition has two distinct properties: (1) it is shiny white and (2) it has a very high ash fluid temperature (>1700 °C). The latter explains why kaolinite-rich coals are very suitable for fixed-bed dry-bottom coal gasification.

2. Experimental

2.1. Determination of clay mineral fractions in coal

Clay minerals in coal (and associated water release) are not easy to determine due to limitations in each characterisation technique, as follows:

2.1.1. Petrographic analysis

The resolution of a light microscope is limited to a few microns [14] and only well crystallized stratified silicate minerals can be identified. Images are measured volumetrically and so must be converted to wt%, and this requires accurate maceral and mineral densities values [13]. However, it is still a useful method when detecting the type of clays that are present.

2.1.2. X-ray diffraction (XRD)

In general XRD can identify the clay crystals in a coal sample, but due to the association of minerals with organic coal matrix, it is not possible to quantify the amount. Furthermore, due to the stratified nature of clays, they tend to be not as evenly distributed as other minerals resulting in variable and uncertain concentration values. Clays can also have significant fractions (especially if treated with water) of amorphous material which are not detected using XRD. An additive measuring technique could be applied to determine the crystalline fraction of certain clays i.e. measuring clay peaks of the raw coal and adding stepwise defined amounts of well-known clay standards thus calculating the concentration from the magnification of the peak. However, the total clay content is not measurable by XRD even after low-temperature ashing [7].

2.1.3. X-ray fluorescence (XRF)

XRF is used as standard elemental analysis for ash composition determination in the oxide state which requires ashing of the sample. So far, these data represent the frequently available figures to estimate the clay content of a sample [15]. The difficulty is to assign the Al_2O_3 and SiO_2 fraction to the correct clay mineral [16].

2.1.4. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA)

The identification and quantification of clays using their thermal and/or gravimetric decomposition peaks is a common method [2]. However, if the organic coal matrix is linked to the clays, the pyrolysis products overlap with the release of clay water and, hence, no clear measurement is possible. A DTA/TGA analysis after ashing could yield reasonable results but requires elaborate low-temperature ashing procedures (<370 °C in air or special plasma furnace) [8].

2.1.5. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) and back-scattered electron (BSE) detectors

These techniques produce an image of a polished cut cross-section of raw coal particles immersed in wax or resin. After the coal particles are identified, the elemental composition of the particles is determined yielding i.e. a grey-scale image for BSE method. A minerals database is used to determine the particular minerals which are assigned to each particle visualized by different colors. From the color distribution, it is possible to calculate the area % of each mineral species. If the density is known, the mass percentage of minerals can be calculated. Since such analysis is commonly used to determine which minerals can be liberated from the coal grains and finally separated by density separation (washing), it is called Mineral Liberation Analysis (MLA). The Mineral Liberation Analyser© system from JKTech was initial launched in the late 90s [17] using this technique for mineral identification. Further publications describe the improvements to the technique moving beyond BSE mapping [18]. Around the same time, CSIRO spun out the QEM SCAN© system using similar hardware which was initially commercialized by Intellection [19]. Both systems benefitted from the increased processing speeds of modern PCs and the speed and automation of SEM microscope systems, which hampered earlier attempts in the 70s [20] and 80s [21].

The quantitative ability of the QEM SCAN/MLA systems in converting volumetric (vol%) measurements to weight based (wt%) values is entirely reliant on the accurate identification of the mineral phase, the accuracy of mineral density values, adequate and representative sampling (during block preparation) and finally the sampling size (during analysis). This issue is discussed further in Section 2.2. The separation of touching particles has also been a significant challenge for image analysis based approaches, particularly when the particles themselves are quite irregular [22]. The sampling and separation of mineral based particles has been previously discussed by JKTech and others [17–19].

2.2. MLA procedure

In this study, the estimation of clay mineral decomposition water based on XRF oxide ash composition is compared to MLA-based composition.

In order to prepare samples for MLA, a fine-grained coal sample (<1 mm) was fixed in a block and polished according to the following procedure: 1 g of sample was placed in 30 mm diameter mould and heated at 95 °C. It was mixed with carnauba wax flakes and finally cooled down slowly. The specimen was ground using 500 grit SiC paper until plane. Subsequently, it was exposed to 1200 grit SiC for 1 min and polished with 3 µm diamond solution for 4 min followed by 1 µm diamond solution for 2 min. Afterwards, the surface of the polished mounts was carbon coated so as to be ready for introduction to the SEM beam. The SEM used a 20 kV accelerating voltage, 200× magnification and 13 mm working distance. The MLA 'measurement' software was used with the following settings: 200 frames, boundary particles retained, and automatic background removal. The XBSE mode was used (places an X-ray on each grain within every particle of each frame) and a