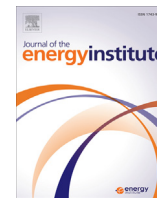




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FT-IR and micro-Raman spectroscopic characterization of minerals in high-calcium coal ashes

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ABSTRACT

Two high-calcium coal ashes were prepared in a muffle furnace at 815 °C. The mineral matter in both coal ashes was characterized by Fourier transform infrared (FT-IR) spectroscopy, micro-Raman spectroscopy, and X-ray diffraction (XRD). The overlapping bands of original FT-IR spectra were resolved into individual ones by using second derivative method. The presence of two most intense absorption bands (1154 and 1120 cm⁻¹) in the original spectra indicate that both coal ashes contain high levels of anhydrite, consistent with the XRD result. The presence of amorphous silica and metakaolinite was found from the second derivative spectra. Calcite and anhydrite in both ashes show marked Raman bands at 1086 and 1017 cm⁻¹, respectively. In addition, the Raman intensity of anatase in both ashes is very strong, due to the high polarizability of Ti–O–Ti. FT-IR and micro-Raman spectroscopy are complementary for the identification of anhydrite in coal ashes. Moreover, a combination of both spectroscopic techniques can provide more information on mineral composition and structure as compared to XRD, since XRD fails to identify the presence of amorphous silica, metakaolinite, and anatase.

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1. Introduction

Coal is a complex, heterogeneous mixture of organic and inorganic constituents. The inorganic constituents in coal mainly consist of crystalline minerals, amorphous minerals, and fluid matter [1]. Since mineral matter plays an important role in coal conversion such as combustion, gasification, and pyrolysis, much work has been done on the identification and characterization of minerals in coal and coal ash by various analytical techniques over the past two decades [1–4]. Of the techniques for identification of minerals, X-ray diffraction (XRD) is most widely used because it provides qualitative and quantitative information about mineral composition. Recently, however, Fourier transform infrared (FT-IR) spectroscopy has received much attention because it has been successfully used for the analysis of both organic functional groups [5–7] and mineral composition (e.g., clay, sulfate, slag, pottery, and oil shale) [8–12]. In fact, FT-IR spectroscopy has two advantages over XRD for the identification of minerals. First, it allows for identification of both crystalline and amorphous phases, especially the mineral transformations upon heating. Second, FT-IR spectroscopy can clearly distinguish the origin of water molecules, such as structural water, coordinated water, and zeolitic water.

Over the years, FT-IR spectroscopy has also been employed to analyze the mineral compositions of coal and coal ash. The difference spectrum obtained by subtracting the absorption spectrum of demineralized coal from that of raw sample was shown to be useful in the analysis of mineral matter in coal [13]. Mukherjee and Srivastava [14] reported the band shift of mineral transformation in coals from kaolinite (1025 cm⁻¹) to quartz (1081 cm⁻¹) upon heating at 850 °C. Bai et al. [15] analyzed the FT-IR spectra of coal ashes prepared at 1300 and 1400 °C under reducing conditions. They found that the strongest absorption band located in the range 1100–950 cm⁻¹ was related to asymmetric Si–O–Si or Si–O–Al stretching vibration of aluminosilicate. Mozgawa et al. [16] investigated four fly ashes from coal-fired power plants in Poland using FTIR spectroscopy. FTIR technique was found to be useful in both describing the structure of mineral phase and identifying individual components of ash. The amorphous aluminosilicates show a shoulder band at 915 cm⁻¹, although these

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minerals are not identified by XRD [16]. Fernández-Jiménez and Palomo [17] also conducted FT-IR spectroscopic studies on coal ash. They observed that the strong characteristic bands of aluminosilicate occurred in the range similar to that noted by Bai et al. [15]. Han et al. [18] found that obvious kaolinite bands existed in the FT-IR spectra of lignite coals, which was consistent with the relatively high SiO₂ and Al₂O₃ content in the coals. In addition, Painter and co-workers [19] developed a least squares curve-fitting method for the quantitative analysis of the mineralogical composition (e.g., kaolinite, quartz, calcite, pyrite, and illite) of a low-temperature coal ash. They found that FT-IR results were in good agreement with those obtained from XRD. Moreover, the FT-IR method was found to be faster than XRD. A quantitative FTIR method for determination of quartz content in coal ashes has been reported in the literature [20]. This method was associated with the quartz doublet at 800 cm⁻¹. The quantitative results were comparable to the data from an empirical formula based on ash composition.

Since a mineral mixture easily produces overlapping absorption bands in the original spectrum, the resolution of these bands into individual component bands is of great importance for spectral interpretation. Resolution enhancement methods such as derivative spectroscopy and Fourier self-deconvolution are usually employed to resolve the overlapping bands. The second derivative method is the most commonly used and yields sharper bands than the original spectrum. This method has been widely used to determine the overlapping bands of organic functional groups (e.g., aliphatic hydrogen, aromatic hydrogen, and oxygen-containing groups) in coal sample [21,22]. Moreover, this method has been successfully used to acquire detailed mineralogical composition of pottery [11], clay [23], ceramic [24], and wall paintings [25]. However, little attention has been paid to the mineralogical analysis of coal ash by this method.

In addition to FT-IR spectroscopy, micro-Raman spectroscopy is a potentially powerful tool for mineralogical analysis, since it is highly sensitive to the composition and structure of a sample material. Minor or trace impurities in a mineral mixture can be easily detected by micro-Raman spectroscopy [26]. Raman spectra data for a large number of minerals are readily available online in the RRUFF database (<http://rruff.info/>) [27]. In addition, the shape of a Raman band is related to the degree of order. For example, the crystalline minerals generally show relatively sharp bands; however, broad Raman bands are due to amorphous phases or fluorescence. Although much research has been done on the micro-Raman spectroscopic analysis of mineral mixtures such as mine waste [26], cement [28], and pottery [29], few studies have been conducted on the identification of minerals in coal ash by this technique [30,31].

The main purpose of this study is to identify the mineral composition of two high-calcium coal ashes by using FT-IR, micro-Raman spectroscopy, and XRD. The results of a combination of the two spectroscopic techniques were compared with those obtained from XRD in order to demonstrate the wide applicability of both spectroscopic techniques in the characterization of coal ash.

2. Experimental

2.1. Coal samples

Two bituminous coals from Inner Mongolia, China, Shenhua (SH) and Lijiata (LJT) coals, were used in this study. The coal samples were ground and sieved to 58–80 μm. Proximate and elemental analyses were performed on selected coal samples according to the Chinese standards, GB/T212-2008 and GB/T476-2001, respectively. The results of these analyses are given in Table 1.

2.2. Ash sample preparation

The coal ash samples were prepared using a standard method (GB/T212-2008). About 1 g of coal sample was weighed into a crucible and placed in an electrically heated muffle furnace. The coal samples were slowly heated to 500 °C in 30 min and maintained at this temperature for 30 min, followed by heating to 815 ± 10 °C and keeping at this temperature for an additional hour. The resulting ash samples were removed from the furnace and allowed to cool in a desiccator. After cooling, the coal ash samples were collected for further analysis. Bulk elemental composition of the ash samples was analyzed by X-ray fluorescence (XRF), and the results are shown in Table 2. Table 2 shows that both ashes are enriched in Si, Al, Ca, and Fe.

2.3. Mineralogical analyses

In this study, the mineralogical composition of both ashes was identified by using a Rigaku D/max 2550 X-ray diffractometer. This diffractometer was equipped with a 10 kW high-intensity rotating anode (Cu K_α radiation, 5–80°). For the purpose of comparison, FT-IR spectra of both ashes were recorded on a Nicolet iS 10 spectrometer (Thermo Fisher Scientific Inc.) in the range 4000–400 cm⁻¹. Fifty scans were collected from each sample with 4 cm⁻¹ resolution. KBr pellets of coal ashes were prepared with a sample/KBr ratio of 1:100. The total mass was approximately 100 mg to ensure a reasonable signal-to-noise ratio. Background noise and atmospheric suppression were subtracted with OMNIC software. The overlapping bands in the fingerprint region (1600–400 cm⁻¹) were resolved by using second derivative method.

In addition to XRD and FT-IR, micro-Raman spectra of both ashes were acquired by using a LabRAM ARAMIS confocal Raman spectrometer (HORIBA Jobin Yvon) with an Ar⁺ laser (λ = 532 nm) as an excitation source. Micro-Raman spectra were recorded in the range 2000–100 cm⁻¹. The incident beam focused at a 2 × 2 μm spot through an objective with 50× magnification. Typical spectra were obtained

Table 1
Proximate and elemental analyses of test coals.

Sample	Proximate analysis (wt%, air-dried basis)				Elemental analysis (wt%, air-dried basis)			
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	O ^a
SH coal	8.18	7.75	27.91	56.16	67.17	5.06	0.79	11.05
LJT coal	9.98	6.82	30.94	52.26	75.79	4.06	0.80	2.55

^a By difference.

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