THE THERMAL TRANSMISSION BEHAVIOR ANALYSIS OF TWO COAL GANUES SELECTED FROM INNER MONGOLIA IN CHINA

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The differences in the structure and thermal behavior of two coal gangue samples (Z-1 and Z-2) obtained from Inner Mongolia in China were investigated through thermogravimetry-derivative thermogravimetry (TG-DTG), X-ray diffraction (XRD), and Fourier-transform infrared (FT-IR) spectroscopy. The TG-DTG results indicate that the two coal gangue samples present different dehydroxylation temperatures and loss on ignition values. The mineralogy of the Z-1 sample consisted of kaolinite and quartz, whereas that of the Z-2 sample consisted of kaolinite, boehmite, and quartz. The XRD and FT-IR spectra revealed the thermal transmission behavior of the two coal gangue samples when temperature was increased from 300 °C to 1000 °C. The coal gangue samples lost hydration water at a temperature of up to 500°C, and the layer structure collapsed completely as the temperature increased. The typical bands in the FT-IR spectra of the two coal gangue samples are similar, but several differences were observed in the intensity and positions of bands. The intensity of the characteristic bands of boehmite at 3090 and 3280 cm⁻¹ decreased as the temperature increased, and the bands disappeared at 600 °C. The thermal behavior of the coal gangue samples differed because of impurities and mineralogical compositions.

Key words: coal gangue, thermal behavior, dehydroxylation, kaolinite, boehmite

Introduction
Coal is expected to become the predominant fossil fuel in use for at least the next 50 years [1]. However, coal consumption produces a large amount of coal gangue. Coal gangue is the solid waste produced in the process of coal mining and beneficiation, it is sandwiched between coal seam and varies from 10% to 15% depending on mining range and geological conditions [2-4]. In China, the total accumulated stockpile of coal gangue has reached 4.5 billion metric tons [5, 6]. Coal gangue can cause serious damage to the environment, including occupying a large amount of land and farmland and polluting the atmosphere and water. Previously, Querol et al. [7] have conducted field and lab study on spontaneously ignited gangue hills in Yangquan in Shanxi province, China and demonstrated the exacerbation of environmental impact on local soil and water body of spontaneous combustion of gangue hills other than long term weathering. Coal gangue contains various chemical and mineral compositions, and generally contains large amounts of silica, alumina, clay minerals, and carbonaceous minerals [8-11]. The utilization of coal gangue has elicited much attention in China in the past decades.

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The chemical composition of coal gangue varies significantly with different time horizons, regions, and means of mining. The main chemical components of coal gangue are SiO$_2$, Al$_2$O$_3$, and carbon, in addition to TiO$_2$, Fe$_2$O$_3$, CaO, K$_2$O, Na$_2$O, etc. [12-14]. Its mineral components mainly include clay minerals (kaolinite, sericite), quartz, calcite, pyrite, siderite and carbonaceous minerals [15, 16]. The most common and dominant clay mineral in coal gangue is kaolinite. Kaolinite is a 1:1 layered dioctahedral aluminum silicate that belongs to the kaolin group of minerals. The 1:1 layer structure consists of tetrahedral silica units stacked together with octahedral alumina units [17, 18]. The folded layers are connected by van der Waals forces and strong hydrogen bonds involving both Al and Si groups (Al–O–H–O–Si).

The technological applications of coal gangue are based on its physical and chemical properties, structure, composition, and thermal behavior [19-21]. Coal gangue is an important and useful industrial byproduct because of its properties, such as minimal impurities and low carbon content. Coal gangue with minimal impurities has been used utilized in the manufacture of building products, porcelain, refractories, etc. [22]. Most of the studies in recent years focused on structural and textural changes in coal gangue. Thermal treatment can change the physical and chemical properties of coal gangue and provides some information about the thermal evolution of coal gangue because several physico-chemical properties of coal gangue, such as particle size, surface area, and mineralogy are significantly affected by thermal treatment [23]. Zhang et al. [24] thought that the feedstock properties (combustible matter, mineral matter) of coal gangue are different depending on source, coal rank, and coal mining technique and washing technology and feedstock properties affected the change of activation energy with conversion values. High ash coal gangue combustion behavior is not only influenced by combustible matter but also by mineral matter. This effect is most probably due to the heat absorption of mineral matter [25-27]. There is little information about the research of the thermal behavior of coal gangue from different coal seam. Thermal treatment can provide some information about thermal evolution of coal gangue and is necessary for its further application, especially in the filler industry.

This study investigates the structure and behavior of thermal treatment of two coal gangue samples obtained from Inner Mongolia in China through TG-DTG, XRD, and FT-IR. The purpose of the study is to investigate the structural evolution of the chemistry and mineralogy of the two coal gangue samples obtained from different coal seams during thermal treatment.

Experimental

Materials and methods

Two main types of coal gangue exist in the Inner Mongolia coal field: one type is from the roof of the coal seam, and is mainly composed of mud stone, clay or shale powder sandstone. The other one is from tonstein in the coal seam, and is mainly composed of mud stone, carbonaceous mud stone, clay and rock. Two coal gangue sample was collected through drilling hole from the single vertical direction. Samples of the same borehole contain roof and tonstein coal gangue. Two coal gangue samples were obtained from the roof (Z-1) and tonstein (Z-2) of coal mines multiple boreholes in Inner Mongolia. The two coal gangue samples were ground to 200 meshes with a jaw crusher and sieved to a particle size of below 100 µm. The treated coal-gangue samples were heated at 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C for 2 hours at a rate of 10 °C per min in a muffle furnace under an air atmosphere. Related tests and experiments were then conducted. The main chemical component and loss on ignition of the two coal gangue samples are shown in tab. 1.
Table 1. Chemical composition of two coal gangue samples from Inner Mongolia

<table>
<thead>
<tr>
<th>Coal gangue sample</th>
<th>SiO₂ [%]</th>
<th>Al₂O₃ [%]</th>
<th>Fe₂O₃ [%]</th>
<th>TiO₂ [%]</th>
<th>Na₂O [%]</th>
<th>K₂O [%]</th>
<th>MgO [%]</th>
<th>Loss on ignition [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-1</td>
<td>44.313</td>
<td>31.260</td>
<td>0.266</td>
<td>0.820</td>
<td>0.056</td>
<td>0.051</td>
<td>0.050</td>
<td>22.182</td>
</tr>
<tr>
<td></td>
<td>42.264</td>
<td>30.271</td>
<td>0.176</td>
<td>0.746</td>
<td>0.041</td>
<td>0.052</td>
<td>0.043</td>
<td>24.410</td>
</tr>
<tr>
<td></td>
<td>43.214</td>
<td>32.312</td>
<td>0.184</td>
<td>0.823</td>
<td>0.061</td>
<td>0.046</td>
<td>0.053</td>
<td>21.307</td>
</tr>
<tr>
<td>Z-2</td>
<td>33.680</td>
<td>37.569</td>
<td>0.266</td>
<td>0.649</td>
<td>0.076</td>
<td>0.070</td>
<td>0.056</td>
<td>26.610</td>
</tr>
<tr>
<td></td>
<td>35.142</td>
<td>38.571</td>
<td>0.242</td>
<td>0.721</td>
<td>0.064</td>
<td>0.062</td>
<td>0.049</td>
<td>24.148</td>
</tr>
<tr>
<td></td>
<td>32.734</td>
<td>37.531</td>
<td>0.245</td>
<td>0.623</td>
<td>0.061</td>
<td>0.073</td>
<td>0.043</td>
<td>26.648</td>
</tr>
</tbody>
</table>

Characterization

The phase compositions of the raw coal gangue samples before and after thermal treatment were investigated through XRD analysis by using a diffractometer (D/MAX 2500 PC, Rigaku) equipped with a Cu target, Ka radiation source, and slit system, at a scanning speeds of 4° per minute, and scanning range of 2.5-60° (2θ). The tube voltage was 40 kV, and the tube current was 40 mA.

The FT-IR was conducted with a Thermofisher Nicolet6700 spectrometer. The samples were prepared at potassium bromide (KBr) pellets and then ground in an agate mortar. The mixture was pressed into a pellet for the transmittance infrared spectroscopic measurements. The FT-IR spectra of the prepared samples between 400 and 4000 cm⁻¹ were recorded.

The TG-DTG measurements were carried out with Switzerland Mettler Toledo TGA/DSC1/1600HT. The two coal gangue samples were heated from ambient temperature to up to 1100 °C at a heating rates of 10 °C per minute under air atmosphere.

The morphology of the raw and the calcined coal gangue was observed by a cold field emission SEM (S-4800 Hitachi). During the observation, an accelerating voltage of 15 kV was selected, and the resolution was of ±2 nm.

Results and discussion

The XRD

The XRD patterns of the two raw coal gangue samples are shown in fig. 1. The major mineralogical composition of the Z-1 sample is kaolinite and quartz. In addition, The XRD patterns the two raw coal gangue also contains weak diffraction peaks of tridymite, mica, anorthite, and gismondine, etc. The pattern of the Z-1 sample presents several typical strong diffraction peaks of kaolinite (Al₂O₃·2SiO₂·2H₂O) at 2θ = 12.6° and 25°, and the values of these diffractions are 0.701 and 0.353 nm because of the diffraction of the (001) and

Figure 1. The XRD patterns for two raw coal gangue
(002) crystal planes, respectively. The three diffraction peaks with values of 0.407, 0.431, and 0.413 nm at $2\theta = 22^\circ$-$25^\circ$ are due to the diffraction of (020), (110), and (111) crystal surface reflection, respectively. The diffraction peak with a value of 0.350 nm at $2\theta = 26.7^\circ$ is attributed to quartz [28]. The mineral components of the Z-1 sample are relatively pure kaolinite according to the diffraction peaks. The major mineralogical composition of the Z-2 sample is kaolinite and quartz. The identical peak intensity and position are also shown in diffractogram of the Z-2 sample. In the pattern of the Z-2 sample, the characteristic diffractions peaks with values of 0.602, 0.313, and 0.165 nm at $2\theta = 14.7^\circ$, 28$^\circ$, and 55$^\circ$ are attributed to boehmite [29, 30], indicating that boehmite, $\gamma$-aluminum oxihydroxide $\text{AlO(OH)}$, is also the main mineral components. Boehmite is usually a component of bauxite and a mineral uncommon in coal gangue. The boehmite locating in the bottom layers of coal gangue are formed by desilication effect of kaolinite under the action of humic acid. These results reveal the high content of aluminum in the Z-2 sample, thus the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is less than the theoretical value. Boehmite is enriched in the Z-2 sample. The molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the Z-1 sample is less than 2, whereas the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the Z-2 sample is greater than 2, thus indicating the high aluminum content and abundant aluminum minerals in the Z-2 sample. In the pattern of the sample Z-1, the diffraction peak attributed to quartz at $2\theta = 26.7^\circ$ is intense, which indicates that sample Z-1 contains more quartz than sample Z-2. The mineral components of the Z-1 sample are relatively pure kaolinite according to the diffraction peaks. These results are consistent with the chemical analysis results.

**Infrared spectroscopy**

The FT-IR spectroscopy can reveal the molecular structure of coal gangue. Coal gangue is mainly composed of kaolinite. The infrared spectra of kaolinite mainly include characteristic absorption bands of $\text{Si–O}$, $\text{–OH}$, and $\text{H–O–H}$. which contain typical stretching vibration modes of $\text{–OH}$ and $\text{H–O–H}$ in the high-frequency region (3600-3400 cm$^{-1}$) and bending vibration modes of $\text{Si–O}$, $\text{Al–O}$ groups, and hydroxyl groups in the low frequency region (1600-400 cm$^{-1}$) [31]. The FT-IR spectra of the two coal gangue samples are shown in figs. 2 and 3. Differences in the position and intensity of the $\text{H–O–H}$, $\text{–OH}$, $\text{Si–O}$, and $\text{Al–O}$ group vibration modes were observed. These differences may be due to the variations in composition and impurities. Two obvious and similar bands were observed for the two coal gangue samples in the 3500-4000 cm$^{-1}$ region. The bands at 3620 cm$^{-1}$ and 3690 cm$^{-1}$ are approximately attributed to the inner hydroxyl stretching vibration peak and outer hydroxyl stretching vibration. Three bands (3690, 3620 cm$^{-1}$) in the OH stretching region are attributed to kaolinite with mostly aluminum in the octahedral position. The absorption peak at 912 cm$^{-1}$ is attributed to $\text{Al–OH}$ bending vibration [32]. The bands at 1030 and 1120 cm$^{-1}$ are assigned to $\text{Si–O–Si}$ stretching vibrations, indicating that the existence of kaolinite, tridymite, illite and quartz in coal gangue, in agreement with the XRD results.

Figure 3 shows the FT-IR spectra of the Z-2 sample. In the high wavenumber region, in addition to the hydroxyl vibration characteristic bands of kaolinite in the range of 3000-3300 cm$^{-1}$, the bands at 3280 and
3090 cm\(^{-1}\) are associated with the stretching vibration band mode of the hydroxyl of boehmite, and the bands at 746 and 642 cm\(^{-1}\) are associated with the characteristic bands of boehmite that are attributed to the superposition band of Al–O stretching vibration and bending vibration absorption of kaolinite and boehmite [9]. The band at 1610 cm\(^{-1}\) is attributed to Si–O–Si asymmetric stretching vibration and O–Si–O stretching vibration mode [4], indicating the existence of illite. The result corresponds to the result of XRD.

**Thermal analysis**

The TG-DTG curves of samples Z-1 and Z-2 are shown in figs. 4 and 5. An endothermic peak exists at approximately 100 °C in the Z-1 sample, with a mass loss of 1.87\%. The peak is attributed to the adsorbed water in the TG-DTG curves of the Z-1 sample in fig. 4. The endothermic peak presented at 519.3 °C with a mass loss of 14.43\% is associated with the dehydroxylation of coal gangue. However, the endothermic peak presented at 501.5 °C with a mass loss of 22\% is associated with the dehydroxylation of the Z-2 sample in fig. 2. The theoretical loss of the structural water of kaolinite is 14.4\%. The loss on ignition of the Z-2 sample is larger than that of the Z-1 sample. The mass loss of Z-2 sample is larger than the theoretical value of the structure of water in kaolinite, which indicates that dehydroxylation reaction and carbon loss of kaolinite and boehmite occurred [16]. This result is in agreement with the loss on ignition results of the two coal gangue samples. The differences in the thermal behaviors of the two coal gangue samples were distinct, which indicates that mineral compositions exerted a significant influence on the thermal behavior of the samples.

**Mineral transformation and structural evolution of the two coal gangue samples during calcination**

The XRD patterns of two thermally treated coal gangue samples calcined at 300 °C to 1000 °C are shown in figs. 6 and 7. The diffraction peak shape of the two samples calcined at 300 °C
and 400 °C is similar to that of the two raw coal-gangue samples. The change in the XRD diffractogram of the Z-1 sample at different temperatures is shown in fig. 6. The diffraction peak with a value of 0.709 nm at 2θ = 12.4° gradually weakened as the temperature increases. At a calcination temperature of 600 °C, the diffraction peaks of kaolinite completely disappeared through the removal of the inner hydroxyl structure, which may be due to the destruction of the crystal face (001) the formation of an amorphous substance, and transformation of kaolinite to metakaolinite [4, 16]. The diffraction peak with a value of 0.350 nm at 2θ = 25° is attributed to quartz. The diffraction peak attributing to kaolinite, gismondine, mica, anorthite, etc. at 20-40 °C basically disappeared. The diffraction peaks of quartz still exist as the temperature increases, which could be attributed to the generation of active SiO₂ through the decomposition of clay minerals, such as metakaolinite and illite.

Figure 7 shows the diffraction patterns of the Z-2 sample at different temperatures. The diffraction peak with a value of 0.701 nm at 2θ = 12.6° gradually weakened as the temperature increased and disappeared at 600 °C. The characteristic diffractions peaks of boehmite with values of 0.602 and 0.313 nm also gradually weakened and disappeared at 700 °C, thus revealing the destruction of the crystal face of boehmite and the formation of an amorphous substance. The diffraction peak at 20-40 °C basically disappeared and the diffraction peaks of quartz also disappeared, indicating that sample Z-1 contains more quartz than sample Z-2. The result corresponds to the result of XRD analysis of raw samples.

The crystallinity of two gangue was gradually decreased and the symmetry changed worse as the temperature increases, which causing diffraction peak broaden and weaken. The coal gangue has transformed from the crystalline to amorphous state.

The FT-IR spectra of the Z-1 sample at different temperatures are presented in fig. 8. The intensities of the two bands at 3690 and 3620 cm⁻¹ gradually decreased, and the bands disappeared at 700 °C as the temperature increased in the 3000-4000 cm⁻¹ region. This result indicates that the hydroxyl groups of coal gangue were removed compared with those in uncalcined coal gangue. The intensity of the bands at 914 cm⁻¹ gradually decreased, and the band disappeared at 800 °C. This result indicates that the breakages of Al–OH as the temperature increased. The intensity of the bands at 1110, 1030, and 1010 cm⁻¹ also gradually weakened and presented a wide band at 1090 cm⁻¹ as the temperature increased. This result indicates that the dehydration reaction of illite and kaolinite result in metakaolinite [33, 34]. These results are associated with the depolymerization and collapse of the tetrahedral silica structure [4].
The FT-IR spectra of the Z-2 sample at different temperatures are presented in fig. 9. The changes in high wavenumber are similar to those of the Z-1 sample, and the changes in the bands are also attributed to the evolution of the hydroxyl group. The bands at 1110 and 1010 cm\(^{-1}\) gradually weakened as the temperature increased, and a wide band emerged when the temperature was 700 °C, which indicates the generation of new substances. The bands at 3280 and 3090 cm\(^{-1}\) gradually weakened with the increase in temperature and disappeared at 600 °C, indicating that the hydroxyl of boehmite of in the Z-2 sample was removed as the temperature increased. The intensity of the bands at 793 and 744 cm\(^{-1}\) also gradually weakened with the increase in temperature. The absorption peak at 1090 cm\(^{-1}\) became wider, indicated the generation of new substances. These results are associated with the dehydroxylation and collapse of the layer structure.

The SEM images of the coal gangue calcined at 800 °C are presented in figs. 10(a) and 10(b). Two coal gangue have no obvious difference from the SEM images. The micro-structure of two coal gangue presented uniform and loose size distribution. The structure turns to irregular and porous when coal gangue heated at 800 °C, in figs. 10(a) and 10(b), which may be caused by the dehydroxylation of kaolinite and phase change to metakaolin. Calcined coal gangue is basically loose because of the component volatilization and fame expansion.

Figure 8. The FT-IR spectra for Z-1 samples heated at different temperatures

Figure 9. The FT-IR spectra for Z-2 samples heated at different temperatures

Figure 10. The FT-IR spectra for Z-1 and Z-2 samples heated at 800°C; (a) Z-1 coal gangue and (b) Z-2 coal gangue
Conclusions

The TG-DTG, XRD, and FT-IR spectroscopy were utilized to study the difference in the structure and thermal behavior of two coal gangue samples obtained from Zhungeer. The TG-DTG data indicate that the two samples have different dehydroxylation temperature and loss on ignition values. The mineralogy of the Z-1 sample consist of kaolinite and quartz, whereas that of the Z-2 sample consist of kaolinite, quartz, and boehmite. The Z-2 sample contains high aluminum content and abundant aluminum minerals, and Z-1 sample contains more quartz than the sample Z-2 sample.

This result corresponds to the TG-DTG data. The XRD and FT-IR spectra revealed that the structural changes in the two coal gangue are due to impurities and mineralogical compositions when temperature is increased from 300 °C to 1000 °C. The hydroxyl groups of the two coal gangues were removed at 700 °C. The typical bands in the FT-IR spectra of the two coal gangue samples are similar, but several differences in positions and intensities were observed. The micro-structure of calcined coal gangue presented uniform and loose size distribution. The results of this work can provide theoretical basis for extraction of aluminum in coal gangue from Inner Mongolia.

Acknowledgment

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References


