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Effect of calcination condition on the microstructure and pozzolanic activity of calcined coal gangue

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ABSTRACT

In this paper, a systematic study was conducted to investigate the influence of calcination conditions including grinding time of raw material, temperature, holding time and heating rate on the pozzolanic activity of calcined coal gangue (abbreviated as CCG hereinafter). Furthermore, the changes of mineral composition, chemical structure and morphology of coal gangue during calcination were characterized by means of thermogravimetric-differential scanning calorimeter (TG-DSC), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) analyses. The results show that heating temperature affects directly the mineralogy and crystallinity of CCG. Kaolinite in coal gangue transforms into metakaolin which is an irregular and amorphous phase as calcined at 600 °C–800 °C because of the dehydroxylation of Al–(O,OH) octahedrons together with the depolymerization of Si–O tetrahedrons. The amorphous metakaolin is of high pozzolanic activity; however, it will lose its activity due to the recrystallization into mullite when heating temperature is over 1000 °C. The pozzolanic activity of CCG is mainly dependent on the non-crystallizing degree of kaolinite after calcination.

1. Introduction

Coal gangue is a complex industrial solid waste discharged when coal is excavated and washed in the production course of coal mine. Its major chemical compositions are SiO_2 and Al_2O_3, and major mineralogical compositions are kaolinite, illite, and quartz. The amount of coal gangue accumulated in China has already reached 3.8 billion tons; moreover, the stockpile of coal gangue is increasing at a rate of 0.2 billion tons per year (Gu, 1997). Existing coal gangue in such a large quantity has occupied a lot of land and caused many serious environmental problems.

Presently, two major methods are applied for the reuse of coal gangue: combustion for power generation (Liu and Liu, 2010) and used as building materials, such as cement admixture (Li et al., 2006) and goaf backfill (Yao and Sun, 2012), among these, cement admixture accounts for the largest proportion of the utilization of coal gangue. However, the raw gangue cannot be utilized directly as cement admixture due to its weak pozzolanic activity (Zhang, 2006). Therefore, improving the pozzolanic activity of coal gangue is a critical process in its utilization as building materials. Many studies have been carried out on the activation of coal gangue containing clay minerals and thermal treatment is the most common method used by these researchers (Buchwald et al., 2009; Seiffarth et al., 2013).

The main reaction that happened in the activation of coal gangue is dehydroxylation of clay minerals such as kaolin and the formation of metakaolin, which is an amorphous mineral with high pozzolanic activity (Siddique and Klaus, 2009; Dellisanti and Valde, 2012). Thermal treatment with a low temperature or short holding time gives metakaolin which is not very reactive and contains residues of kaolin and carbon, however, a temperature over 925 °C leads to the beginning of crystallization and a decline of pozzolanic activity (Konan et al., 2009). Therefore, in order to get a better pozzolanic material, the calcination condition such as temperature, holding time and heating rate should be controlled accurately.

In this paper, we systematically investigated the influence of calcination conditions including fineness of raw material, temperature, holding time and heating rate on the pozzolanic activity of CCG. Furthermore, the mineral composition, chemical structure and morphology of CCG under different temperatures were characterized comparatively by means of XRD, FTIR and SEM analyses.

2. Experimental procedures

2.1. Raw materials

Coal gangue used in this study was obtained from JingYang Coal Washing Plant, which is located in Baotou City of China. The mineralogical

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phase was characterized by XRD as shown in Fig. 1. It indicates kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and quartz ($SiO_2$) are the major crystallized minerals presented in the raw coal gangue. The chemical composition and physical properties of raw coal gangue are presented in Table 1. The mineral compositions of raw and calcined coal gangues are shown in Table 2. The result shows that the raw coal gangue has a high purity of kaolinite which can be calcined to prepare a high reactive pozzolan.

2.2. Thermal treatment

The raw samples were wet ground with a stainless steel rod mill at a rotation speed of 400 rpm for 10 min, 20 min, 30 min and 40 min. The specific surface area (measured by N_2 adsorption multi-point BET method) and fineness (residue on 30 μm sieve, %) of ground samples are presented in Table 3. The ground samples were dried and then calcined at different temperatures (400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C) with different heating rates (10 °C·min^{-1}, 30 °C·min^{-1}, 50 °C·min^{-1} and 70 °C·min^{-1}) for different holding times (1.0 h, 1.5 h, 2.0 h and 2.5 h). The influences of grinding time, calcination temperature, holding time and heating rate on the pozzolanic activities of calcined products were evaluated by Chapelle test.

2.3. Test methods

The chemical compositions of samples were performed on a PANalytical X-ray fluorescence analyzer.

Thermogravimetric and differential thermal analysis (TG-DSC) were obtained simultaneously using a Mettler Toledo 851 instrument. In order to separately analyze the combustion reaction of carbon and dehydroxylation of kaolin during the thermal treatment of coal gangue, two ground raw samples were heated from ambient temperature to 1200 °C at a rate of 10 °C·min^{-1} under 50 mL·min^{-1} air and argon gas, respectively.

The mineralogical phase and crystal structure were characterized by X-ray diffraction using a Rigaku D/max-RB powder diffractometer, with Cu Kα radiation (40 kV; 100 mA).

The chemical structures of CCG under different roasting temperatures were analyzed by Fourier transform infrared spectra using a Spectrum-One, Perkin Elmer FTIR spectrometer in absorbance mode with KBr pellet technique (1–2 mg sample with 200 mg KBr).

SEM test was carried out on a Hitachi SC-2500 scanning electron microscope for observing the morphology and microstructure of CCG.

The pozzolanic activity was determined according to the Chapelle test. A gram of CCG was mixed with 1 g of $Ca(OH)_2$ and 200 mL boiling water. The suspension was boiled for 16 h and the free $Ca(OH)_2$ was determined by means of sucrose extraction and titration with a HCl solution(Kakali et al., 2001).

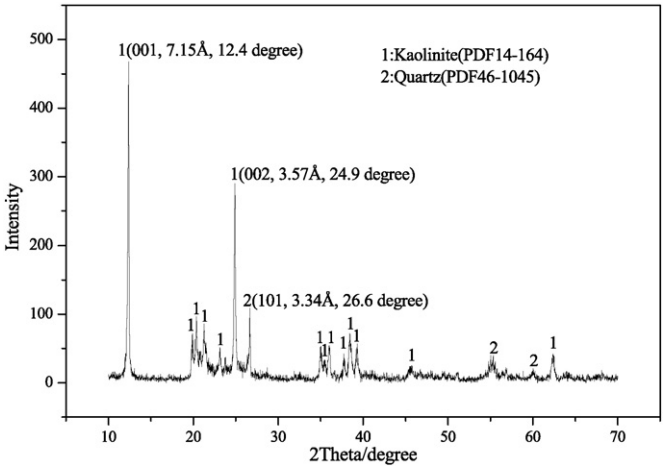

Fig. 1. XRD pattern of raw coal gangue.

Table 1
Chemical composition and physical properties of raw coal gangue.

SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	TiO_2	LOI	Specific gravity g·cm^{-3}
%									
39.08	31.06	0.38	0.24	0.26	0.16	1.20	0.98	26.60	2.16

3. Results and discussion

3.1. TG-DSC measurement

Fig. 2 presents the TG-DSC curves of coal gangues under air and Ar gas separately. Calcining coal gangue in absence of oxygen (in Fig. 2(b)), the weight loss of 15.2% is attributed to the decomposition of minerals such as kaolinite and dolomite; and the combustion of carbon and organic matter causes the weight loss to increase by 11.4% under aerobic calcination (in Fig. 2(a)).

The endothermic peak presented at 500 °C in Fig. 2 is contributed by the dehydroxylation of kaolinite and formation of metakaolinite; the exothermic peak at 1000 °C is due to the transformation of metakaolinite into mullite. It is deduced that kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot H_2O$) in coal gangue begins to decompose into amorphous metakaolinite ($Al_2O_3 \cdot 2SiO_2$) at 500 °C and transforms to the crystallized mullite ($3Al_2O_3 \cdot 2SiO_2$) when temperature reaches up to 1000 °C (Ilic et al., 2010). The two thermal induced processes can be described by the following reactions:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \overset{500^\circ C}{\rightarrow} Al_2O_3 \cdot 2SiO_2 + 2H_2O\,(g) \quad (1)$$

$$3(Al_2O_3 \cdot 2SiO_2) \overset{1000^\circ C}{\rightarrow} 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2. \quad (2)$$

The exothermic peak at 600 °C in Fig. 2(b) may be caused by the combustion of carbon and organic matter, which indicates that higher temperature is needed for the removal of carbonaceous minerals than amorphization of kaolinite. This scheme is represented by the following chemical equations:

$$C + O_2 \rightarrow CO_2 \quad (3)$$

$$C_mH_n + \left(2m + \frac{1}{2}\right)O_2 \overset{600^\circ C}{\rightarrow} mCO_2 + \frac{1}{2}nH_2O. \quad (4)$$

3.2. XRD analysis

XRD patterns of calcined coal gangues under different temperatures are presented in Fig. 3. Kaolinite and quartz are the two major crystallized minerals in the uncalcined coal gangue. Kaolinite is a hydrous layer silicate clay mineral. The structural unit of kaolinite consists of a Si-O tetrahedral sheet and an Al-O(OH) octahedral sheet (Frost, 1997). The crystallinity of kaolinite in the coal gangue can be evaluated on the basis of XRD background in the range 2θ = 20–30°and the width

Table 2
Mineral compositions of raw and calcined coal gangues.

Raw coal gangue	Content (%)	Calcined coal gangue	Content (%)
Kaolinite	78.55	Metakaolinite	92.09
Quartz	2.55	Quartz	3.47
Carbon and organic matter	15.64	Else	4.44
Else	3.26		