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Improvement on pozzolanic reactivity of coal gangue by integrated thermal and chemical activation

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HIGHLIGHTS

- Cement containing 56% of activated coal gangue was produced and applied.
- Improved reactivity of coal gangue contributes to generated amorphous substances.
- Energy consumption for producing it could save 90.7 (kg coal equivalently /ton).

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ABSTRACT

In order to effectively utilize coal gangue and its calorific value (4180–12,540 kJ/kg), coal gangue was converted into energy-saved cement by activating at 800 °C with an integrated thermal and chemical activation method. Microanalysis with XRD and NMR indicates that improved pozzolanic reactivity for coal gangue contributes to the mineral phase change with amorphous status during thermal and chemical activation process. In the chemical activation process, amorphous materials composed of Q^3(0Al), Q^3(1Al) and Q^0 units were formed from parts of aluminosilicate minerals (quartz and K-feldspar). With the physical and mechanical testing, it shows that $CaSO_4$ + CaO is the most effective additive during the chemical activation, which is a non-equilibrium reaction between coal gangue and $CaSO_4$ + CaO during calcination process. A prototype plant in cement industry also proofs these results. Eco-cement containing 56% of activated coal gangue had been successfully produced for road pavement application with a 28-days concrete compressive strength of 35.9 MPa. Compared with the traditional clinker producing process, energy consumption for producing activated coal gangue could save 90.7 kg/ton equivalently, which is due to its low calcination temperature at 800 °C and calorific value (about 6688 kJ/kg) of the coal gangue.

1. Introduction

Coal gangue is a typical inert solid waste discharged when coal is excavated and washed in the production. In China, the total of accumulative stockpile of coal gangue has reached 4.5 billion metric tons [1]. Their major mineralogical compositions are stable aluminosilicate minerals at the ambient conditions, such as quartz and feldspar. Such large quantities of the solid waste have not only occupied a great deal of land but also become harmful in initiating geologic hazards and land degradation [1].

A traditional method to improve pozzolanic reactivity of coal gangue is directly calcination, i.e. a thermal activation method. Studies [2–5] showed new generated amorphous reactive SiO_2 and Al_2O_3 from clay minerals are contributed to improvement of its reactivity. But this method is inefficient to activate inert aluminosilicate minerals, which are the main components of coal gangue.

Many studies on improving pozzolanic reactivity of inert solid wastes were conducted in the past decade [6–10]. Iron ore tailings could be activated to increase its reactivity by calcinations process with mixing into lime [6]. Quartz in coal gangues could engage in hydration reaction when sulfates were mixed in hydrated paste [7]. Potash slate could have pozzolana activity though calcinations process with mixing sodium carbonate [8]. Coal gangue could be activated more efficiently by calcination with mixing into lime or red mud rather than with simple calcinations process [9,10].

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The above discussions indicate that it is feasible to activate the inert solid waste by both calcination and corrosion process. In this paper, in order to effectively utilize coal gangue and its calorific value of 4180–12,540 kJ/kg, an integrated thermal and chemical activation method was investigated. X-ray diffraction (XRD), Nuclear magnetic resonate (NMR), thermodynamic analysis and chemical activation experiment on feldspar were conducted to illustrate the mechanism of reactions in this activation process. And an industrial prototype test using this activation method was completed on a cement clinker production line with daily capacity of 1500 ton and its energy consumption was analyzed.

2. Experimental materials and methods

2.1. Materials

Coal gangue was obtained from Fangshan district, Beijing. Tangshan Iron and Steel Group Co. Ltd. and Beijing Xingang cement plant supplied granulated blast-furnace slag and clinker, respectively. Feldspar was from Zibo Ceramic Raw Materials Company. Chemical composition and physical properties of the raw materials are presented in Table 1. Chemical compound CaO, $CaCO_3$, $CaSO_4$ and $CaCl_2$ from Beijing Modern Orient Fine Chemical Ltd were used as activation additives, and gypsum ($CaSO_4$) with 92 wt.% anhydrite from Nanjing Jiangsu were used in preparing coal gangue based cement.

2.2. Raw material activation procedure

In this procedure, coal gangue was firstly crushed and then respectively mixed together with different activation additives at a ratio of 18:2 for additive of CaO, and 18:1:1 for each compound additive of $CaSO_4$ + CaO, $CaSO_4$ + $CaCO_3$ and $CaSO_4$ + $CaCl_2$. Subsequently, each mixture was ground in a laboratory ball mill (Mz-3 type made by Beijing Hongding Machinery Co., Ltd.) for 15 min. Then, with a water-to-solid ratio of 0.15, each mixture was shaped to 8–10 mm diameter spheres and calcined for 3 h at 700 °C, 800 °C, 900 °C and 1000 °C. After the calcination process, they were removed from the furnace respectively, followed by a cooling process to room temperature in air, and were ground in the laboratory ball mill to the Blaine's specific surface area of 425 m^2/kg.

Experiment on integrated activation of feldspar was conducted to research mechanism of chemical activation process. Feldspar, $CaSO_4$ and CaO were mixed at a weight ratio of 180:17:3. At such ratio, the mole ratio of CaO:$CaSO_4$ is about 14 which equal to their ratio in Eq. (4). Then the mixture was calcined at 800 °C for 3 h.

2.3. Testing conditions

Compressive strengths of blended eco-cement mortars were tested to evaluate the pozzolanic reactivity of coal gangues according to Chinese Standard GB/T17671-1999 [11]. Two types of coal gangue (by thermal activation only and by thermal and chemical activation together) were used in the experiment. The designed proportion of the coal gangue based eco-cement contains coal gangue of 56 wt.%, slag of 25 wt.%, clinker of 15 wt.% and gypsum of 4 wt.%. In this test, water to cement ratio was 0.50 and cement to sand ratio was 1:3. Mortar specimens in size of 40.0 mm × 40.0 mm × 160.0 mm were cured in a moist cabinet at 95% humidity and 20 °C for 24 h, and then demoulded and placed back in the cabinet under the same curing conditions. At 28 days, three cubes were tested in compression and the presented results are averages of the three replicates.

The chemical analysis for coal gangue was performed with the X-ray fluorescence (Model XRF-1700, Shimadzu, Japan) analyzer. XRD (Model D/max-RB, Rigaku, Japan) analysis was conducted in the 2θ ranging from 5° to 70° with a scanning rate of 4°/min, and X-ray diffractions were recorded with a Cu Kα diffractometer. ^{29}Si and ^{27}Al magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy were acquired by using a BRUKER-AM300 Solid State NMR. The resonance frequency of ^{27}Al and ^{29}Si at a magnetic field strength of 7.05 T were 78.20 and 59.62 MHz, respectively. Fourier transform infrared (FTIR) spectra were acquired using a Spectrum GX, PE FTIR spectrometer in absorbance mode using the KBr pellet technique (1–2 mg sample with 200 mg KBr). DSC and TG (Model STA409C/3/F, NETZSCH, German) was performed under the standard conditions by heating the samples from 40 to 1000 with a 10 °C/min heating rate.

Table 1
Chemical composition and physical properties of raw materials by XRF.

Oxides (wt.%)	Coal gangue	Slag	Clinker	Feldspar
SiO_2	45.57	33.59	21.94	71.79
Al_2O_3	16.35	14.37	5.27	15.31
CaO	1.93	38.32	66.09	2.85
Fe_2O_3	6.02	1.11	2.96	1.11
Na_2O	1.44	0.18	0.3	2.95
K_2O	2.85	0.11	0.7	5.28
MgO	1.56	8.43	0.88	0.28
TiO_2	0	0.85	–	0.16
SO_3	0.04	2.26	0.31	0.03
LOI	24.24	0.44	0.67	–
Specific surface, Blaine (m^2/kg)	–	400	400	–

3. Experimental results

Compressive strength of mortars prepared from different activated coal gangues are shown in Fig. 1. 800 °C is the optimal activating temperature at which the highest 28-days compressive strength could be achieved. At each temperature from 700 °C to 1000 °C, 28-days compressive strength of mortars composed of integrated activated coal gangue is higher than that of mortar composed of thermal activated coal gangue.

Moreover, among mortars composed of integrated activated coal gangue, the ones with activation additives of $CaSO_4$ + CaO and $CaSO_4$ + $CaCl_2$ have the rather higher 28-days compressive strength, and that with $CaSO_4$ + CaO has the highest 28-days compressive strength of 39.6 MPa at 800 °C. The activated coal gangue

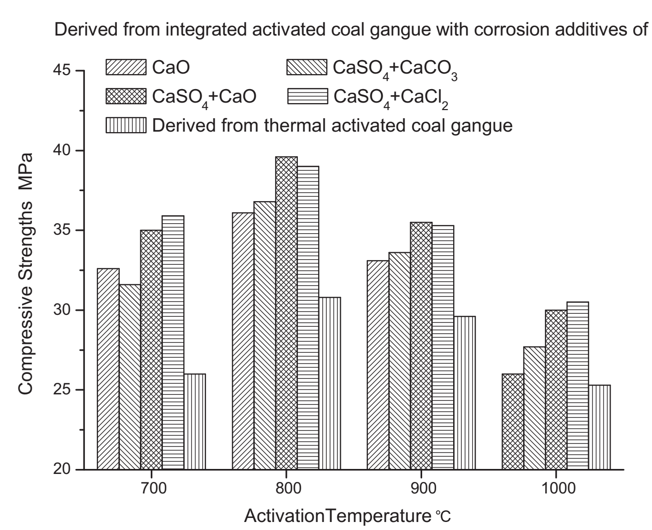

Fig. 1. 28-Days compressive strength of mortars prepared from different activated coal gangues calcined at 700, 800, 900, 1000 °C.