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Research paper

Assessment of pozzolanic activity of calcined coal-series kaolin

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ABSTRACT

Coal-series kaolin (from the Yichang region of China) was tested as a potential pozzolanic material to be used in the cement and concrete industry. Thermal treatment was used to activate the raw coal-series kaolin (RCK). Phase identification before and after calcination was studied by X-ray diffraction and Fourier transform infrared spectroscopy. The pozzolanic activity of calcined coal-series kaolin (CCK) was tested by two direct methods, modified Chapelle and Frattini tests, and one indirect method, strength activity index. Aside from thermal treatment, grinding process for CCK was also used to evaluate the effect of particle size distribution on pozzolanic activity. The results showed that pozzolanic activity of CCK was greatly influenced by dehydroxylation and particle size. The modified Chapelle test overestimated pozzolanic activity in the low pozzolanic region (0–1300 mg CH/g CCK), and was suitable for complete dehydroxylation samples. The Frattini test accurately assessed CH consumption by pozzolanic reaction, and the strength activity index confirmed the physical effect contribution to CS enhancement at earlier stage and pozzolanic reaction contribution to enhanced microstructure (pore and grain size refinement) and hence improved mechanical strength of cementitious material at later stage.

1. Introduction

Pozzolans are defined as "a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties" (ASTM C618, 2013). The pozzolanic reaction slowly consumes calcium hydroxide (CH) and forms a C-S-H and C-A-S-H gel which refines pore size distribution and enhances mechanical properties and durability (Tironi et al., 2013, 2014). Partial replacement of pozzolans into mortar and concrete is encouraged due to reduced CO_2 emission and energy consumption (Tironi et al., 2012b). Pozzolans are obtained from geo-resources (volcanic glasses, zeolites, tuff, and calcined clay) or from industrial by-products (silica fume; fly ash; sludge ash; rice husk ash etc.) (Lawrence et al., 2005; Agarwal, 2006; Chakchouk et al., 2009; Donatello et al., 2010a). Generally, clays do not exhibit pozzolanic behaviour without thermal activation.

Coal-series kaolin, a by-product of seam deposition in coal accumulating basins has large reserves (about 3.8 billion tonnes in China) and is rich in SiO_2 and Al_2O_3 (Querol et al., 2008; Ji et al., 2013). Hence it could be a suitable pozzolan for mortar and concrete. Thermal activation (550–900 °C) is essential for application of coal-series kaolin to cement industry, since raw coal-series kaolin has low pozzolanic activity (Cao et al., 2016). The main reaction occurring in thermal activation is dehydroxylation of kaolinite and formation of the metakaolinite amorphous phase, AS_2. The amorphous phase has high pozzolanic activity and will react with CH produced by cement hydration to form C-S-H, C-A-H and C-A-S-H gel (Murat, 1983),

$$AS_2 + 6CH + 9H \rightarrow 2C-S-H + C_4AH_{13} \text{ (calcium aluminate hydrate)} \quad (1)$$

and

$$AS_2 + 3CH + 6H \rightarrow C-S-H + C_2ASH_8 \text{ (strätlingite)} \quad (2)$$

The pozzolanic activity of calcined coal-series kaolin (CCK) is assessed by modified Chapelle and Frattini tests, which measure CH consumption by the pozzolanic reaction, and strength activity index (SAI), an indirect method which measures the change of physical-mechanical property related to the pozzolanic reaction (Donatello et al., 2010b).

The modified Chapelle test is standardized and performed in an aqueous lime-metakaolin system, over 16 h at 90 °C with continuous stirring, and quantifies the amount of CH fixed by the metakaolin. The Frattini test assesses CH consumption by the pozzolanic reaction in mixed cement and pozzolan, and SAI measures the compressive

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strength of the blended cement and discriminated the pozzolanic reaction contribution to the strength enhancement.

The objective of this study was to assess pozzolanic activity for calcined coal-series kaolin (CCK) by modified Chapelle test, Frattini test and strength activity index. The effect of calcination temperature and particle size on pozzolanic activity was also evaluated and correlations between test results were investigated. The mineralogy, thermal properties, crystallinity and phase transformation of coal-series kaolin were also determined to investigate the activation procedure mechanism.

2. Materials and methods

2.1. Raw coal-series kaolin

The raw coal-series kaolin (RCK) used in this study was obtained from the Yichang region in Hubei province, China. The RCK Blaine specific surface and median diameter, d_{50}, were 638 m^2/kg and 12.7 μm, respectively.

2.2. Calcined coal-series kaolin

Calcined coal-series kaolin (CCK) was prepared by calcining 200 g RCK in a crucible at different temperatures in the range 500–900 °C with 2 h holding time using a muffle furnace. The CCK was then cooled to room temperature at ambient conditions to avoid crystallization of amorphous metakaolin (Shvarzman et al., 2003). Samples prepared by calcining at 800 °C were wet ground by planetary mill for 0.5, 1, 2, 4 and 8 h to obtain ground samples with different size fractions.

2.3. Characterizations

Chemical compositions of RCK and CCK were determined using the Axios advanced spectrometer (PANalytical.B.V Dutch).

Organic matter in RCK samples was characterized by total organic carbon (TOC) using a TOC–LCSH analyser (Shimadzu, JPN) combined with the SSM–5000A module for solid samples.

Mineralogical composition of RCK and CCK was determined by powder X-ray diffraction (XRD) using a rotation anode high power X–ray diffractometer (RU–200B/D/MAX–RB, Rigaku Corporation, JPN) employing CuKα radiation (λ = 0.154 nm, 40 kV, 50 mA) over scanning range 2θ = 5–70° with step width 2°min^{-1}.

Thermogravimetric analysis was performed on a STA449F3 simultaneous thermal analyser (Netzsch, Germany) with 10 K/min and air atmosphere to collect TG, DTG and DSC curves.

Fourier transform infrared (FTIR) spectra of the samples were scanned on a Nicolet 6700 (Thermo Fisher Scientific, USA) using KBr diluent over 4000–500 cm^{-1}.

Particle size distribution was measured by a laser particle size analyser (BT-9300S, Bettersize Instruments Ltd., CN) using a dilute suspension conditioned with dispersants (analytically pure sodium hexametaphosphate).

2.4. Pozzolanic activity

Pozzolanic activity of CCK samples was measured by modified Chapelle test, Frattini test and SAI.

The modified Chapelle test was conducted according to the French method NF P18–513 (NF P18–513, 2010; Ferraz et al., 2015), where 1 g CCK was reacted with 2 g CaO in 250 mL of deionized water at 90 °C for 16 h. Non-reacted lime was extracted by sucrose solution and measured by titration. The result was expressed in mg CH consumed by g CCK (mg·CH/g CCK).

The Frattini test was performed according to the procedure described in EN 196–5, 2005 standard. Test samples were prepared by mixing 16 g ordinary Portland cement CEM I 42.5 R (OPC) with 4 g CCK, and then adding 100 mL freshly boiled deionized water. Table 1 shows OPC chemical composition and Table 2 shows the estimated Bogue potential phase composition of OPC. After preparation, samples were placed into sealed polyethylene container and left for 3, 7 and 28 days at 40 °C. At test time, the samples were immediately filtered under vacuum through a Buchner funnel using drying double filter paper and then allowed to cool to room temperature. The filtrate was analyzed for [OH] by titration using 0.1 mol/L HCl solution with methyl orange indicator and for [CaO] by pH adjustment to 12.5, followed by titration with 0.03 mol/L EDTA solution using Patton and Reeders indicator. This test compares the [CaO] and [OH] contained in an aqueous solution that covers the hydrated sample at 40 °C for a given time (3, 7 and 28 days) with the CH solubility curve in an alkaline solution at the same temperature. CCK is considered as active pozzolan when [CaO] and [OH] in solution is down the solubility isotherm.

The compressive strength (CS) of blended cement was assessed on mortars cubes (4 × 4 × 16 cm) made with standard sand (1:3) and water/blended cement of 0.5 (EN 196–1). The blended cement consisted of 88% w/w OPC and 12% w/w CCK (12% replacement level guarantees the largest CS enhancement from Table 3). Strength activity index (SAI) was calculated as the ratio of the compressive strength of the blended cement mortar to the strength of the reference ordinary Portland cement mortar at the same age. After the compressive test, fragments at the mortar centre were immersed in ethyl alcohol for 24 h and dried at 40 °C overnight. Bulk sand particles were removed by carefully crushing and screening through a 75 μm sieve, and the material was characterized by TG analysis.

Table 1
Chemical composition of OPC, RCK and CCK (T = 800 °C).

Oxide	OPC	RCK (%)	CCK (%)
SiO_2	20.14	49.03	52.38
Al_2O_3	4.63	34.18	42.23
Fe_2O_3	3.08	0.73	0.89
CaO	62.62	0.20	0.20
K_2O	0.93	0.12	0.17
TiO_2	0.31	1.72	2.20
SO_3	3.58	0.23	0.27
Na_2O	0.16	–	–
MgO	2.35	–	–
LOI	1.63	13.50	1.41
TOC	–	0.20	–

Table 2
Estimated Bogue potential phase composition of OPC.

Clinker	Mass fraction (%)
C_3S	56
C_2S	16
C_3A	7
C_4AF	9

Table 3
Compressive strength (CS, MPa) for different replacement levels of CCK (T = 800 °C) into OPC mortar.

Replacement level	Compressive strength (MPa)		
	3 days	7 days	28 days
0	21.0	31.0	41.0
6	22.1	34.5	43.9
12	23.2	37.7	48.7
18	21.0	31.8	44.8
24	19.3	30.8	42.3
30	18.5	29.8	40.8