Construction and Building Materials 171 (2018) 558–565

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Influence of calcined coal-series kaolin fineness on properties of cement paste and mortar

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HIGHLIGHTS

- The influence of CCK fineness on properties of cement paste and mortar is studied.
- Finer CCK particles have high pozzolanic activity and consume more CH.
- Finer CCK leads denser texture and decreased massive tabular CH structure of paste.
- Three effects of CCK cause the enhanced properties of cement paste and mortar.

ARTICLE INFO

Article history:
Received 22 November 2017
Received in revised form 12 March 2018
Accepted 15 March 2018

Keywords:
Calcined coal-series kaolin
Fineness
Properties
Cement
Paste and mortar

ABSTRACT

Three calcined coal-series kaolin (CCK) samples, with same chemical and mineral composition but different fineness (Blaine specific surface of 760, 1369 and 1856 m^2/kg), were used as pozzolan in cement paste and mortar and the influence of their fineness on materials properties was systematically studied by several methods and analyses. The pozzolanic activity of CCK is evaluated by Frattini test and confirmed by mechanical properties of blended mortars. TG–DSC analysis, complemented with XRD analysis, determines the type and the amount of hydrated phases at different ages to evaluate the influence of fineness on hydration properties of blended paste. Finally the microstructure of blended paste containing finer particles is observed by FESEM analysis. The results show that the finer particles have higher pozzolanic activity, leading to the more consumption of $Ca(OH)_2$ and the more production of additional C–S–H, C–A–H and C–A–S–H, which compact the paste and mortar texture and remarkably enhance the mechanical strength at later ages (after 7 days). The finer particles also have higher physical effect to accelerate the cement hydration and slightly increase mechanical strength, $Ca(OH)_2$ content and combined water at earlier ages (before 7 days).

1. Introduction

Coal-series kaolin, a by-product in the coal mining and dressing procedure with large reserves (about 3.8 billion tons in China), is rich in chemical constituents of SiO_2 and Al_2O_3 and hence can be used as pozzolan into cement mortar and concrete after calcination [1]. The partial replacement of calcined coal-series kaolin (CCK) into mortar and concrete will slowly consume the calcium hydroxide (CH) and form the additional C–S–H, C–A–H and C–A–S–H, leading to the refinement of pore size distribution, enhancement of the mechanical properties and durability [2–4]. The utilization of pozzolan into mortar and concrete will decrease the cement content and hence reduce CO_2 emission and energy consumption, which is eco-friendly and encouraged by government [5].

According to Murat [6], the formed amorphous phase metakaolinite (AS_2) after calcination of coal-series kaolin performs high pozzolanic activity and can react with calcium hydroxide which produces by cement hydration to form C–S–H, C–A–H and C–A–S–H gels as follows:

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

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

The factors of AS_2 affecting the properties of cement paste and mortar were researched in the past, such as replacement level, calcination temperature, holding time, location, degree of crystallinity and fineness [7–12]. Frías and Cabrera [7] studied the influence of replacement level on the porosity and degree of hydration and found that the addition of 15%–20% MK performed an important improvement in the porosity accompanying with the reduction

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https://doi.org/10.1016/j.conbuildmat.2018.03.117
0950-0618/

of the average pore diameter and gel porosity and then a good correlation between porosity and degree of hydration has been established. Arikan et al. [8] adopted thermal treatment to activate three kaolin clays from different locations with different chemical composition and fineness for different holding time and then found that the optimal quality for metakaolin can be manufactured by the thermal treatment of raw kaolin with 74% of kaolinite at 750 °C without the intermediate beneficiation stage. Mermerdaş et al. [9] used four Turkish kaolins to enhance the compressive strength after calcination and provided similar behavior to that of the commercial metakaolin, which improved the concrete strength especially at 15% replacement revel. Taylor-Lange et al. [10] reported the phase transformation of three kaolin clays at 650–930 °C and indicated that as the amorphous content of calinced clays increased, it consumed more portlandite and the compressive strength increased. Alujas et al. [11] researched the pozzolanic reactivity and hydration behaviour of low grade kaolinitic clays after calcining at different temperature and demonstrated that highest pozzolanic reactivity is reached when calcined at 800 °C and a combination of a filler effect at early ages and the pozzolanic reaction greatly impacted the hydration behaviour. Kakali et al. [12] compared the Greek kaolin with commercial kaolin to evaluate the effect of mineralogy on the pozzolanic activity of calcined kaolin and revealed that well-ordered kaolinite is transformed into less reactive metakaolinite.

In consideration of the influence of calcined clays fineness on the properties of cement paste and mortar, most publications adopted the kaolin ores from different localities with different fineness, but the differences of chemical and mineral composition and degree of crystallinity was ignored. Therefore an identical metakaolin only with different fineness was obtained by milling calcined coal-series kaolin with different time in our work to ensure the same chemical and structural composition. Then the influence of calcined coal-series kaolin finess on pozzolanic activity, setting time, mechanical properties, phase identification, $Ca(OH)_2$ content, combined water and morphology was systematically studied by several methods and analyses.

2. Materials and methods

2.1. Materials

The used calcined coal-series kaolin (CCK) samples with different fineness were prepared from one type raw coal-series kaolin (RCK) from Hubei province in China by thermal treating at 800 °C for 2 h and then milling different time, which ensured the same chemical and structural composition. The Blaine specific surface (Blaine SS) of CCK samples with different fineness was 760, 1369 and 1856 m^2/kg, respectively and d_{50} of these CCK samples was 14.1, 6.4 and 3.8 μm, respectively. The particle size distributions of the three CCK samples were displayed in Fig. 1. Based on our previous work [13], XRD results showed that the main valuable mineral in RCK was kaolinite, which associated with a small amount of quartz, anatase, feldspar and pyrophyllite. In addition the thermal treatment of RCK guaranteed complete dehydroxylation and no recrystallization of CCK, which was concerned as a high pozzolanic material. The chemical composition of RCK was displayed in Table 1.

2.2. Preparation of cement paste

The blended pastes were prepared by mixed ordinary Portland cement (OPC, type: CEM I 42.5 R) and CCK samples with 12% replacement level for 4 min at a water/blended cement of 0.5. Then the blended pastes were curing at 20 °C with 95% relative humidity for 1, 3, 7, 14, 28 and 90 days. The fragments at the blended pastes centre were collected by cracking blended pastes and immediately immersed into ethyl alcohol for 24 h and dried at 40 °C overnight. Also, the reference paste was also prepared for comparison. The chemical composition of OPC was displayed in Table 1, its Blaine specific surface was 340 m^2/kg and its particle size distribution was also displayed in Fig. 1.

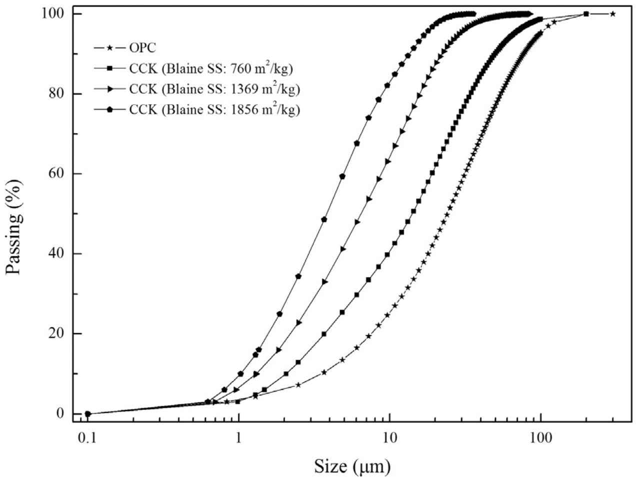

Fig. 1. Particle size distribution of OPC and CCK.

Table 1
Chemical composition of OPC and CCK.

Oxide (%)	OPC	RCK	Clinker[a]	Mass fraction[a] (%)
SiO_2	20.14	49.03	C_3S	56.1
Al_2O_3	4.63	34.18	C_2S	15.5
Fe_2O_3	3.08	0.73	C_3A	7.1
CaO	62.62	0.20	C_4AF	9.4
K_2O	0.93	0.12		
TiO_2	0.31	1.72		
SO_3	3.58	0.23		
Na_2O	0.16	–		
MgO	2.35	–		
LOI	1.63	13.50		

[a] Estimated Bogue potential phase composition of OPC.

2.3. Characterizations

2.3.1. Pozzolanic activity of CCK

Frattini test was used to character pozzolanic activity of CCK according to the procedure described in EN 196-5 standard [14]. In this method, test samples were prepared by mixing 16 g OPC with 4 g CCK and then adding 100 mL freshly boiled deionized water. After preparation, samples were placed into sealed polyethylene container and left for 3, 7 and 28 days in on oven at 40 °C. At the test time, the samples were filtered immediately under vacuum through the 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 solubility curve for CH in an alkaline solution at the same temperature. CCK is considered as active pozzolan when the [CaO], [OH] in the solution is down the solubility isotherm.