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Improving the pozzolanic activity of metakaolin by urea intercalation technique

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HIGHLIGHTS

- Metakaolin prepared from urea-intercalated kaolin possesses at least 10% higher pozzolanic activity than normal metakaolin.
- Urea-intercalated kaolin presents lower dehydroxylation temperature and less inert component formation at high temperature.
- Calcination increases the fineness of urea-intercalated kaolin but reduces that of original kaolin.

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ABSTRACT

The aim of this study was to improve the pozzolanic activity of metakaolin used as mineral additive in concrete by urea intercalation technique. A precursor, urea-kaolin (U-kaolin) with the intercalation degree of 92%, was prepared by evaporating the solvent from suspension containing original kaolin (O-kaolin) and urea. Two series of metakaolin were obtained by calcining the O-kaolin and U-kaolin at nine different temperatures from 550 °C–950 °C for 2 h. The pozzolanic activity of the two series of metakaolin were evaluated and compared by Fixation of Calcium Hydroxide (FCH) and mortar strength as well. In addition, X-ray diffraction, Fourier Transform Infrared Spectroscopy, Thermogravity-Differntial Scanning Calormetry, Brunauer-Emmett-Teller method and Scanning Electron Microscopy were also applied to study the microstructure of the precursor and mechanisms for the pozzolanic activity improvement. The results show that the pozzolanic activity of metakaolin calcined by U-kaolin is 15% higher in the FCH test and 20% higher in cement mortar strength test than the normal one when the calcination temperature is 800 °C. U-kaolin presents lower dehydroxylation temperature due to the weakened interlayer attractive force, and forms less inert component at high temperature due to the looser structure of calcined products. The joint effects of intercalated urea molecules in making precursor and calcination process result in looser structure and higher specific surface to improve of the pozzolanic activity.

1. Introduction

With the climate change and global warming, greenhouse gas emission in construction and building materials manufacturing has been widely concerned. Due to the fact that cement production is responsible for 5%–8% of the global CO_2 emission, more and more researchers dedicate to develop alternative and environmental friendly building materials. Industrial by-products, like fly ash (FA) and ground granulated blast-furnace slag (GGBS), are nowadays widely used in concrete due to the environmental effects as well as the improvement of performance of concrete [1–8]. Low CO_2 emission cement such as calcium sulfoaluminate and binders based on C_2S polymorphs (Ca-Si-Bi) or hydraulic calcium silicates (celitement) were also studied in depth [9–14]. But before the novel building materials are available in application, to achieve the better performance and better durability in construction with less materials is also an important way for green-manufacturing and sustainable development in the construction industry. High performance mineral additives, such as silica fume (SF) and metakaolin (MK) can not only reduce the amount of cement in concrete, but also significantly improve the mechanical properties and durability of concrete, have been applied widely in high performance concrete [9–14]. Nowadays, high performance mineral additives

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are becoming an indispensable composition in high performance concrete for better performance and longer service life.

Kaolin is a type of clay that mainly consists of kaolinite. It is a layered silicate mineral with1:1 layered silicon tetrahedral sheets and aluminum octahedral sheets. The layers are combined by hydrogen bonds and Van der Waals force. Kaolin transforms into metakaolin by dehydroxylation at 550 °C–900 °C. During the calcination process, the structural water dehydrates and the crystalline phase transforms into amorphous phase. Thus, metakaolin possesses high pozzolanic activity, the capability to react with calcium hydroxide in hydrated cement and to form additional hydration products that can enhance performance of cementitious materials. The use of metakaolin as high performance mineral additive in cement-based materials is now wide spread [15–19].

In order to do more with less, different methods were applied to improve the pozzolanic activity of different type of mineral additives according to its characters. Grinding is always adopted for GGBS and rice husk to obtain a refined particle size to improve the pozzolanic activity [20,21]. Air classification or hydraulic classification is usually used to classify FA to get better quality FA. However, the above refining methods are not fit to MK, because MK particles are very small (average particle size always approximately to several micrometers) and easy to form flocs [22]. Further grinding cannot much refine it regardless of tremendous energy consumption. Classification by sieving and air flow is also inefficient because of large amount of formed flocs. Therefore, other methods should be proposed to refine the particle size of MK to improve its pozzolanic activity.

In recent years, kaolin modification attracts more and more attentions in academic researches. Due to the layer structure of kaolinite, some small molecules (as guests) with high polarity can directly intercalate into its interlayer space, such as urea, dimethylsulfoxide, formamide, potassium acetate and ammonium acetate, etc.[23–31]. These polarized molecules break the hydrogen bonds, which are built between oxygen atoms from silicon tetrahedral sheets and hydroxygens from aluminum octahedral sheets, and form new hydrogen bonds. Thereby the molecules intercalate into interlayer and hold stably. After the polarized molecules enter the structure, the interlayer space of kaolinite expands, thus the structure disorder increases [32,33] and the interlayer bonding force weakens [31,34]. Then, the kaolinite delaminates to smaller particles. The dispersibility and surface area of kaolin are increased, and the performances of kaolin are also improved. Many researchers have proved that the original kaolinite can be exfoliated to form nanotubes or nanoscrolls by multiple-step displacement intercalation [35–39]. It consistently supports that using intercalation methods can refine kaolin particle size. Due to the refined particles size, the MK derived from intercalated product may possess higher pozzolanic activity. But, using multiple-step displacement (the method to prepare kaolinite nanoscrolls) may be not practical to obtain a precursor to produce MK used in concretes due to the great increase in cost.

There are many reports focusing on the possibilities and applications of kaolin intercalated complex in a wide variety of fields, such as toxic ions absorber, precursors of nanocomposites and nanohybrids, paper coating agent, etc. [38,40–44]. But few literatures on promoting the pozzolanic activity of metakaolin by intercalation technique are found at present. Due to the exfoliation of kaolinite layers and increased disorder during intercalation process, it may have the great potential to improve pozzolanic activity of metakaolin. The purpose of this research is to improve pozzolanic activity of metakaolin by using urea-kaolin intercalation technique and to develop a high performance mineral additive for construction and building materials. U-kaolin was prepared as precursor and calcined at different temperatures to obtain metakaolin. Compressive strength combined with the Chapelle test followed NF P18-513 was used to evaluate the pozzolanic activity of metakaolin from the perspective of mechanical properties and calcium hydroxide consumption. Multiple analytical techniques were also employed to study the mechanisms involved.

2. Materials and experiments

2.1. Materials

Commercial available original kaolin (O-kaolin), with an average particle size of 5 μm, was supplied by Maoming Kaolin Science and Technology Co. Ltd. in Guangdong Province of China. Ordinary Portland cement (OPC) of grade 42.5 was obtained from Huaxin Cement Co. Ltd. of China. The chemical compositions of O-kaolin and cement by X-ray fluorescence (XRF) are shown in Table 1. The urea was A.R. chemical reagent manufactured by the Sinopharm Group Chemical Reagent Co. Ltd. of China. The fine aggregate was ISO standard sand. Anaphthalene-based superplacticizer was used as a chemical additive to adjust the workability.

2.2. Experiments

2.2.1. Synthesizing the U-kaolin

Urea, distilled water and kaolin were mixed by the mass proportion of 1:1.2:1 in a beaker firstly. Then, the unsealed beaker was transferred into a water bath kettle setting at 70 °C after mixing. To avoid sedimentation, the mixture was artificially stirred to be homogenized every 6 h in the first 48 h. Since the constant evaporation, the urea crystallized from the mixture around in 48 h. Then the beaker was removed from the water bath and aged for 4 days at ambient temperature. After that, some deionized water was added to dissolve all urea crystal and the suspension was followed by centrifuged and the product was washed by distilled water for three times and dried at 60 °C in an oven for 24 h, resulting the U-kaolin. The upper clear liquid can be reused in the intercalation process.

2.2.2. Evaluation of the pozzolanic activities of metakaolin

Two series of metakaolin, M series (metakaolin derived from O-kaolin) and UM series (metakaolin derived from U-kaolin), were prepared by calcining O-kaolin and U-kaolin in a muffle furnace at 550 °C, 650 °C, 700 °C, 750 °C, 800 °C, 850 °C, 900 °C, 950 °C for 2 h, respectively. In this study, the M600 in M series presented the metakaolin calcined from O-kaolin at 600 °C, while the UM600 in UM series was marked as the metakaolin calcined from U-kaolin at 600 °C. During the calcination, the heating rate was 10 °C/min until the target temperature reached, and then the samples were kept at the target temperature for 2 h. After that, the samples were removed from the furnace and cooled at room temperature.

Table 1
Chemical compositions of O-kaolin and cement (wt%).

Oxide	CaO	SiO_2	Al_2O_3	Na_2O	K_2O	Fe_2O_3	SO_3	MgO	P_2O_5	L.O.I
Kaolin	0.07	47.91	37.69	0.27	0.51	0.65	0.11	0.10	0.23	12.13
Cement	58.18	21.25	5.67	0.20	0.62	3.16	3.66	2.41	0.09	3.95