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Potential large-volume beneficial use of low-grade fly ash in magnesia-phosphate cement based materials

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ABSTRACT

Fly ash is a waste produced during combustion of coal that is a significant fossil fuel source for electricity production. Main beneficial use of fly ash has been defined in cement and concrete industry. However, low-grade fly ashes (LGFA), due to their high carbon content and low glass content, can hardly be used in making cement or concrete. Magnesia-phosphate cement (MPC) is a promising but costly binder material for utilizations in repair works of degraded infrastructure and some functional applications. Low-grade fly ash is possible to be consumed in making LGFA-MPC binder, which will undoubtedly reduce the cost and bring additional environmental benefit. In this paper, an MPC paste with the magnesia-to-phosphate molar (M/P) ratio of 8 and a water-to-solid (W/S) ratio of 0.2 is selected as the reference, and a LGFA is used to replace 20%, 40% and 60% of the solid phase by volume, respectively, to examine this possibility. The compressive strengths of the four pastes are measured following the increasing ages, and the water resistance indices of them are also evaluated. The results show that the higher the fly ash replacement, the lower the compressive strength at all ages, but the better the long-term water-resistance. Based on a three-limit theory, the effect of fly ash replacement on compressive strength is explained, and it is proved that the fly ash is more than an inert filler. The influence of fly ash on water resistance is also explained through a microstructural analysis.

1. Introduction

Coal fly ash, a waste product in coal fired power plants, is produced with extremely large volumes worldwide. In America, one of the two most significant electricity sources is coal, sharing 33% of total electricity generation in 2015 [1]. Correspondingly, an American Coal Ash Association (ACAA) survey showed that in 2015, at least 117 million tons of total coal combustion products (CCPs) were produced in electric utilities. Among CCPs, more than 44 million tons of coal fly ash was produced, and only 54 percent (24 million tons) was beneficially used [2]. Meanwhile, the amount of fly ash was projected to be 54.6 million tons in 2033 [3]. Therefore, broadening the ways of utilizing coal fly ash beneficially in large-volume is in urgent need. Nowadays, fly ash is recycled mainly in cement and concrete industry, as a partial replacement of Portland cement [4,5], a clinker additive [6], or the predominate binder in a geopolymer concrete [7,8]. The economic value of fly ash is poor for these applications ($\leq$15 $/ton) [9]. Aiming to enlarge its economic value, Class F fly ash has been studied and proved for its effectiveness as a neutralization and metal fixation reagent for hazardous acidic waste [10] and low level radioactive waste [11]. However, for all above applications, the high aluminum-silicate glass content in fly ash is preferred, since the glass content is correlated positively to the cement hydration ratio [12] and the effectiveness of neutralization and fixation [13]. Limited mass applications of low-grade fly ash have been reported. Herein, low-grade fly ash indicates ashes with low aluminum-silicate glass content, or high carbon content, or other defects that cannot fulfil the requirements of ASTM C618. It is also named as “off-spec” fly ash by the Electric Power Research Institute [14]. Enabling low-grade fly ash as supplementary cementitious materials will definitely increase the beneficial consumption of fly ash in construction materials.

Portland cement has been the governing binder in contemporary concrete since it was patented in 1824. The global cement production was 4.1 G tons in 2015, a 24% increase with regard to that in 2010 [15]. The Portland cement industry is being criticized for its energy-intensive consumption and associated greenhouse gas emission, not to mention that Portland cement is not the perfect binder in all construction applications because of its long setting time and deterioration in severe environments. It is thus a common interest in cement and concrete industry to seek low-energy, low-CO_2, and high-performance

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Table 1
Chemical compositions of magnesia and fly ash (%).

	MgO	CaO	SiO_2	Fe_2O_3	MnO	P_2O_5	Al_2O_3	SO_3	K_2O	TiO_2	LOI
Magnesia	95.10	1.60	1.94	0.68	0.13	0.24	0.31	–	–	–	–
Fly ash	–	4.63	51.58	7.45	0.15	–	27.90	1.37	1.41	1.84	3.67

binders to replace Portland cement, either for general construction purposes or in special applications.

It must be highly desirable if the above-mentioned two problems can be solved simultaneously, i.e. to develop high-performance alternatives of Portland cement by consuming low-grade fly ash. We propose to achieve this goal using a magnesia-phosphate cement (MPC) matrix. MPC is also termed chemically bonded ceramics, which has been drawing increasingly more attention as an alternative cementitious material in pavement and structural repairs and cold weather construction, owing to its advantages of fast setting, ability to set and harden at temperatures as low as −20 °C, high early strength, little shrinkage, and low permeability patch with good durability [16]. Compared with Portland cement, the production of MPC consumes 60% less energy [17] and releases six times less CO_2, which makes it much more environmental friendly [18]. The main barrier of MPC's large-scale application is that its cost is much higher than Portland cement. To solve this problem, on the one hand, low-grade or by-product magnesia can be used in preparation of MPC [19,20]; on the other hand, fly ash can be added to replace the solid phases in MPC [21]. A few studies have been carried out to reveal the effects of fly ash, either class F or class C, on properties of MPC based materials, and to reveal the interaction mechanisms between fly ash and MPC. Some found that the incorporation of fly ash reduced the strength of MPC-based paste or mortar, and they tended to believe that fly ash acted as an inert filler in the multi-component system [20–23]. However, some other researchers have concluded that fly ash can improve the strength and water-resistance of MPC-based materials, more or less, due to a potential secondary reaction [24–27]. In a recent publication, Xu et al. [28] pointed out that the contradictory conclusions in the previous studies could be attributed to the differences in mixture design method, magnesia-to-phosphate ratio, and chemical composition of fly ash. They also deduced that fly ash should be chemically active in the MPC system. Gardner et al. [25] investigated the reaction mechanism, based on a hypothesis that the aluminosilicate glassy fraction in fly ash is the active component and reacts with MPC. However, they were not successful in clearly revealing the mechanism. So far, the role of low-grade fly ash in MPC has not been studied yet. According to Ding and Li [22], no matter which component in fly ash is active, the requested degree of reaction of fly ash in MPC to improve performance is low [22]. Therefore, we expect that low-grade fly ash can also be used in this system without significant performance compromise.

In this paper, the effects of low-grade fly ash incorporation on the properties of MPC paste are investigated preliminarily. A magnesium potassium phosphate cement (MKPC), which is a member of the MPC family, is taken as the reference, and a low-grade fly ash is used to partially replace the solid components of the MKPC by volume (up to 60%). The compressive strengths of different pastes are measured following the increasing ages, and the water resistance indices of them are also evaluated. The mechanisms of the effects of fly ash are explained based on a theoretical calculation and phase characterizations in the light of X-ray diffraction (XRD), mercury intrusion porosimetry (MIP), Fourier transform infrared (FT-IR) spectroscopy and backscattered electron (BSE) imaging.

2. Experimental investigation

2.1. Materials and mix proportions

In experiments, the reference MKPC paste was made from dead burnt magnesia powder, powder KDP (potassium di-hydrogen phosphate), borax and water. The magnesia powder was supplied by Jinan Magnesia-Carbon Bricks Plant Co. Ltd., Jinan, China, and was calcined under 1400 °C for 4 h and then milled into a powder with a Blain fineness of 285 m^2/kg and a maximum particle size of 150 μm. The KDP and borax were both chemical reagents. The densities of magnesia and KDP are 3.58 g/cm^3 and 2.34 g/cm^3, respectively. In the reference MKPC paste, the magnesia-to-phosphate molar ratio (M/P) was 8, the water-to-cement mass ratio (W/C) was 0.2 (cement here means the combination of magnesia and KDP), and borax was added as a reaction retarder at a level of 4% by weight of magnesia. In fly ash incorporated pastes, fly ash was used to replace specific volume fractions, i.e. 20%, 40% and 60%, of the solid phases in the reference paste. This replacement strategy keeps the water-to-solid volume ratios constant in all mixtures. However, the water-to-solid mass ratio (W/S) is changed because the particle density of fly ash is different from that of MKPC. A low-grade fly ash was used in this work. Its glass content is ~40%, which is much lower than the required level by ASTM C618. The used fly ash has a Blain fineness of 400 m^2/kg, an average particle density of 2.4 g/cm^3, and a LOI (loss on ignition) of 3.67. The chemical compositions of the magnesia and fly ash used in this study are given in Table 1, and the particle size distribution curves of magnesia, KDP and fly ash are shown in Fig. 1. The mix proportions of the pastes are shown in Table 2. Pastes are denoted as "FA∗∗V", where FA stands for fly ash, ∗∗ indicates the fly ash replacement ratio in percentage, and V denotes the volume based replacement. In this way, FA00 V denotes the reference paste, and FA40 V the paste with a fly ash replacement of 40%.

2.2. Sample preparation and tests

For preparation of the paste samples, the powder components were dry-mixed firstly for 1 min, which was followed by a mixing with water

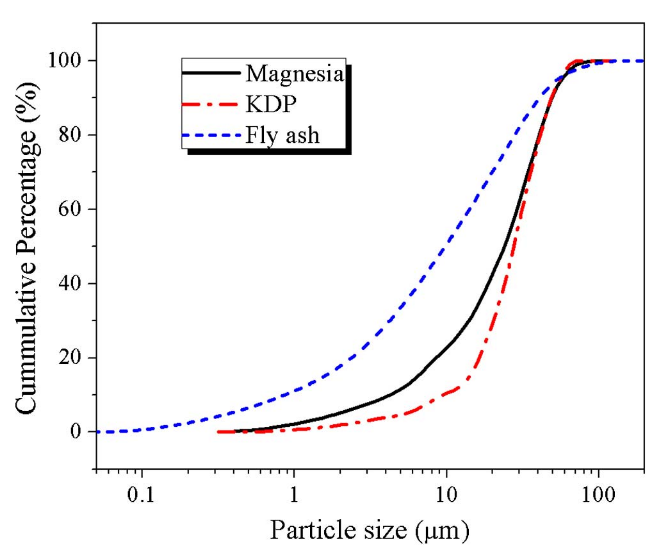

Fig. 1. Particle size distribution curves of magnesia, KDP and fly ash.