ARTICLE IN PRESS

Cement and Concrete Research xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Cement and Concrete Research

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

Influence of fly ash and metakaolin on the microstructure and compressive strength of magnesium potassium phosphate cement paste

Liwu Mo[a,b,*], Liming Lv[a], Min Deng[a,b], Jueshi Qian[c]

[a] No. 30 South Puzhu Road, College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211800, China
[b] No. 30 South Puzhu Road, Key State Laboratory of Materials-oriented Chemical Engineering, Nanjing 211800, China
[c] No. 174, Shazheng Street, College of Materials Science and Engineering, Chongqing University, Chongqing 400045, China

ARTICLE INFO

Keywords:
Microstructure (B)
Compressive strength (C)
Fly ash (D)
Metakaolin (D)
Chemically bonded ceramics (D)

ABSTRACT

The influences of fly ash and metakaolin added as substitutions (by up to 50 wt%) of magnesium potassium phosphate cement (MKPC) on the microstructures and compressive strengths of the MKPC pastes were investigated. The results indicate that the aluminosilicate fractions of both fly ash and metakaolin are involved in the acid-base reaction of MKPC system, leading to a preferential formation of irregular crystalline struvite-K incorporated with Al and Si elements and/or amorphous aluminosilicate phosphate products. Metakaolin is more reactive than fly ash in the MKPC system. For the same addition dosage, the MKPC pastes containing metakaolin exhibit higher compressive strengths than the pastes containing fly ash. This is attributed to the formation of more highly reinforced microstructures and denser interfaces between the metakaolin particle and hydration products (e.g. struvite-K) in the MKPC paste containing metakaolin. Addition of 30 wt% metakaolin increases the compressive strengths of MKPC pastes at all test ages.

1. Introduction

Magnesium phosphate cement (MPC) is a type of chemically bonded ceramic produced through the acid-base reaction between MgO and phosphate salts in terms of potassium dihydrogen phosphate and ammonium dihydrogen phosphate. For the magnesium potassium phosphate cement (MKPC), the reaction can be described as Eq. (1):

$$MgO(s) + KH_2PO_4(s) + H_2O(l) \rightarrow MgKPO_4\cdot 6H_2O(s) \quad (1)$$

Compared to the conventional Portland cement, MPC has some advantageous properties of rapid strength development, high strength at early age, excellent adhesive performance, near-neutral pH, small drying shrinkage [1, 2]. It has a wide range of applications, e.g. solidification/stabilization of heavy metal [3], encapsulation of nuclear wastes [4], repair materials [1, 5–8], bone materials [9], etc. Nonetheless, as a repair material, there are some drawbacks hindering its widespread application, which includes (a) poor water resistance, (b) potential volume instability caused by unreacted MgO or unreacted phosphate salts, and (c) low effectiveness on retarding under relatively high environmental temperature or for the use in a mass volume. To improve the properties of MPC, mineral admixtures in terms of fly ash [10, 11], blast furnace slag [10], metakaolin [12], silica fume [13], etc. are normally added into the MPC system. Nonetheless, the influence of mineral admixture on the properties of MPC depends on its type, chemical and physical properties as well as addition dosage.

Normally, fly ash was considered to simply act as a diluent or inert filler in MPC system [13]. The workability of MPC was enhanced by fly ash via the "ball-bearing effect" due to its spherical shape [4, 6]. Combination of fly ash and silica fume in MKPC was reported to improve the water resistance of the MKPC owing to their physical effects on optimizing the pore structure [13]. However, other studies indicated that the addition of fly ash decreased the tensile strength and the residual strength of MPC after high temperature exposure [14, 15]. Recent researches indicated fly ash was reactive in the MPC system [10, 16]. Gardner et al. [10] prepared MKPC blended with either 50 wt% fly ash or ground granulated blast furnace slag (GBFS) at a MgO-to-Phosphate ratio (M/P) of 1.7:1 and a water-to-binder ratio of 0.24. They reported that the dissolution of glassy aluminosilicate phases occurred in both the fly ash and the GBFS under the neutral pH condition of MKPC system according to MAS NMR tests of ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P and ^{39}K. The secondary products forming in the MKPC blended with 50 wt% of fly ash or GBFS were highly enriched in Al and Si, which could potentially lead to the formation of a potassium aluminosilicate phase. Xu et al. [16] prepared MKPC mortars incorporated with fly ash via two different formulation designs by treating fly ash as inert or reactive but with the same water-to-binder ratio of 0.15. In the former formulation,

* Corresponding author at: No. 30 South Puzhu Road, College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211800, China.
E-mail address: andymoliwu@njtech.edu.cn (L. Mo).

https://doi.org/10.1016/j.cemconres.2018.06.003
Received 20 December 2017; Received in revised form 31 May 2018; Accepted 13 June 2018

fly ash was used to replace both MgO and KH_2PO_4 and hence the M/P molar ratio in the designed fly ash/MKPC mortars remained an unchanged value of 8:1. In the latter formulation, fly ash was used to replace MgO only such that the M/P molar ratio in the MKPC mortar was reduced to 4.5:1. It was found that, owing to the chemical reaction of fly ash, the replacement of MgO alone by the fly ash led to better setting behaviour and workability at the fresh stage and higher compressive strengths of MKPC mortars in comparison to the substitutions of both MgO and KH_2PO_4 with fly ash [16]. According to the SEM measurement, fly ash particles were well encapsulated by struvite-K crystals, suggesting good chemical compatibility between them. Moreover, some reaction products of fly ash particles were observed [16]. However, none of the possible reaction products of the fly ash within the MKPC system could be directly observed by XRD and TGA analysis. Wilson and Nicholson [17] suggested that the aluminosilicate glass in fly ash could react with phosphoric acid to form a strong phosphate bonded cement with high mechanical strength and low water permeability.

Metakaolin is a kind of reactive pozzolanic material that has been used in concrete as a supplementary cementitious material, owing to its reactive aluminosilicate component [18, 19]. Additionally it was used as a raw material for not only alkali-based but also acid-based geopolymer, for which the waterglass and phosphoric acid solution were used as the activators respectively [20]. The compressive strength of the phosphate-based geopolymer cement (93.8 MPa) was higher than that of the alkali-activated geopolymer (63.8 MPa) [20]. This was attributed to the formation of berlinite ($AlPO_4$) as a result of the reaction between the products from dealumination of metakaolin (Al^{3+}) and the PO_4 units from phosphoric acid, which reinforced the structure of geopolymer and hence yielded an increase in the compressive strength. Amorphous –Si-O-Si-O-Al- and -Si-O-P-O-Si- in the metakaolin-phosphate geopolymer cement were thought to be formed [20]. Abundant work has been performed on preparing metakaolin phosphate-based geopolymer cement by reacting the metakaolin directly with a phosphoric acid solution, which possesses high mechanical properties [21–25]. For example, Perera et al. [24] prepared a metakaolin phosphate-based geopolymer by mixing metakaolin with H_3PO_4 to cast ⌀ 25 mm × 40 mm cylindrical specimens at a Si/Al ratio of 1 and an Al/P ratio of 1. Two hours after casting, the specimens were cured at 60 °C for 24 h in an oven and then kept in ambient temperature for 14d, and the average compressive strength of the specimens reached 146 MPa. Cao et al. [25] produced a metakaolin phosphate-based geopolymer cement by mixing metakaolin with H_3PO_4 to cast 20 mm cubic paste at a H_3PO_4/SiO_2 ratio of 1.2:1 and a water content of 6.69 wt%, and the geopolymer cement reached a compressive strength of 55 MPa after 7d of curing at room temperature. Besides metakaolin, alumina can also react with phosphate acid to form an amorphous gelatinous substance of aluminum phosphate ($AlPO_4$) at the temperature higher than 150 °C, yielding a dense microstructure [26].

Metakaolin was added as a supplementary cementitious material to modify the properties of magnesium ammonium dihydrogen phosphate cement (MAPC) [12]. As reported by Lu et al. [12], metakaolin was found to prolong the setting time, enhance the mechanical properties, and improve the water resistance of the MAPC [12]. Based on the micro-analysis of XRD and SEM coupled with energy dispersive spectrometer (EDS), they claimed that the improvement on properties of MAPC obtained by the addition of metakaolin was attributed to the formation of a new type of gel product, namely aluminum phosphate ($AlPO_4$), which increased the density of the cement [12]. However, the quantitative analysis on the elements via EDS under the secondary electronic scanning mode might not be very precise. Whether the metakaolin presents similar contributions to the MKPC system has not been revealed, and it would be of interest to further investigate the interplay between the fly ash or metakaolin and the phosphate salts (KH_2PO_4, $NH_4H_2PO_4$) in the MPC system. In addition, it was reported that a small addition of active alumina also facilitated to prolong setting time, enhance mechanical properties and improve water resistance of MPC, owing to the formation of a geopolymer-like material which caused a reduction of porosity [27, 28].

In comparison to the aforementioned metakaolin phosphate-based binders for which the phosphoric solution was used, little work has been performed to investigate the reaction of metakaolin in the MKPC which has a much weaker acid or near neutral pH environment and the corresponding influence on the mechanical properties of the MKPC at long term is unclear. Although the reaction behaviour and mechanism of MPC without addition of mineral additives have been discussed in some previous researches [29–36], that of the MKPC paste containing fly ash/metakaolin as a substitution of MgO and KH_2PO_4, in particular at a high substitution level, have not been well understood. The addition of mineral admixtures, particularly at a high addition dosage, would change the reaction environment (e.g. pH, heat liberation, ion species, etc.) in the MKPC system, and therefore may influence the reaction behaviour, microstructure formation as well as the following strength development of the MKPC. This study aims to investigate the influence of fly ash and metakaolin on the microstructure and compressive strength of MKPC pastes at various substitution levels of 0 wt %, 30 wt% and 50 wt% by the whole weight of MgO and KH_2PO_4. The possible chemical reaction of fly ash or metakaolin involved in the same MKPC paste system was also examined by employing XRD, SEM/EDS as well as NMR. This study will provide some fundamental information to understand the performance of MKPC modified by the fly ash/metakaolin and the relevant mechanism, which is beneficial for further promoting the performance of MKPC.

2. Experimental

2.1. Preparation of MKPC pastes

Dead burnt MgO was provided by Tianyuan Magnesia Powder Co. Ltd. China, which was produced by calcining magnesite under a temperature of 1500 °C. Industrial grade KH_2PO_4 provided by Shifang Dingli Co. Ltd. in Sichuan was used. Borax was used as the setting retarder at a fixed addition dosage of 4.0 wt% by the weight of MgO. Fly ash and metakaolin were used as partial replacements of MKPC. The chemical compositions of the MgO, fly ash and metakaolin are summarized in Table 1. Accordingly, 34.71 wt% Al_2O_3 and 47.84 wt% SiO_2 are contained in the fly ash. For the metakaolin, higher contents of Al_2O_3 and SiO_2 are contained, being 41.08 wt% and 52.77 wt% respectively. In the metakaolin, the components of Al_2O_3 and SiO_2 exist mainly in the form of amorphous aluminosilicate, whereas they present as crystalline phases of mullite and glassy phase of aluminosilicate in the fly ash. In addition, there is a small amount of quartz contained in the fly ash. The particle size distributions of the dead burnt MgO, fly ash and metakaolin were examined via using a laser particle size analyzer (Mastersizer) and the results are shown in Fig. 1.

M/P ratio has a strong influence on the mechanical performance of MPC [37–40]. As reported, the optimum mechanical performance of MKPC was gained at a M/P ratio of 4:1 [38, 39]. In this study, the MKPC mixtures were prepared with a fixed M/P molar ratio of 4:1. Five groups of MKPC paste were cast, in which the fly ash and metakaolin were used as partial replacements of the MKPC in addition to the reference MKPC paste. Table 2 presents the mix proportions of MKPC pastes. Accordingly, two different substitution levels of MKPC with fly

Table 1
Chemical compositions of raw materials/wt%.

Raw material	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	LOI
Magnesia	95.02	1.41	0.74	0.35	0.22	0.39
Metakaolin	0.80	0.40	0.56	41.08	52.77	1.34
Fly ash	0.92	4.41	7.31	34.71	47.84	3.02