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Ceramics International 38 (2012) 6281–6288
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Cementing mechanism of potassium phosphate based magnesium phosphate cement

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Received 21 March 2012; received in revised form 30 April 2012; accepted 30 April 2012
Available online 9 May 2012

Abstract

Magnesium phosphate cements (MPCs) are materials that belong to chemically bonded ceramic materials. They have a wide range of potential applications, due to their superior performance. In this paper, the reaction products and cementing mechanism of magnesium phosphate bonded cement based on the dead burned magnesia and the mono-potassium phosphate (MPP) are investigated. Fine powder and grains of dead burned magnesia were used to prepare pure cement paste and bonding cluster samples, respectively. The cement reaction products and their micro-morphology in the both different samples are examined. The microstructure of specimens is analyzed by SEM, TEM, XDR, and optical microscopy. Struvite of potassium ($MgKPO_4 \cdot 6H_2O$) is observed in the reaction products. According to the analysis, it is found that struvite exists in both crystalline and amorphous form. There is also residual magnesia in the hardened cement paste. By means of microscopy observation, it can be seen that reaction products form around the unreacted magnesia and can develop into a continuum structure, which further produces the hardened paste. Struvite can grow up to form the more perfect crystal in a long term curing age, if large enough space is available during the hydration process.

Keywords: Magnesium phosphate cement; Microstructure; Microscopic analysis; Reaction products

1. Introduction

Magnesium phosphate cements (MPCs) have excellent performance, such as rapid setting, high early strength and high adhesive properties. They are also called as chemically bonded ceramic matereials [1]. These cements have been extensively used as fast repair materials in civil engineering structures [2–5]. They have been drawing more attention in the recent years, because more and more potential applications have been realized, such as in the management of toxic waste [1,6], in the natural fiber composite products [7], in the fiber composites for reinforce concrete structures [8], in sealing of borehole [9], and so on.

MPCs develop its strength by means of a base-acid reaction, involving dead burned magnesia and phosphates. Usually, dead burned magnesia is a raw material for refractory, which is produced by calcination of magnesite, or abstraction from sea water. At a very high temperature, magnesium oxide becomes a highly crystallized mineral, periclase, that shows a moderate ionic potential and a relatively weak basicity. It was proved that periclase works very well with intermediate acid (usually water solution of phosphates), to form a strong binding material. In order to obtain reasonable setting time, some retarders have to be used in the base-acid reaction, usually they are compounds of boron.

In the present paper, the cementing mechanism of MPC based on the reaction of dead burned magnesia and mono-potassium phosphate is studied. It is a new type of MPC in comparison with the traditional ammonium phosphate cement. Previous studies showed that the performance of this new type of cement can be improved by fly ash, an industrial by-product from power station [10,11]. For example, the mortar samples containing 40% fly ash can develop to 36 MPa in compressive strength, but the mortar

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.04.083

sample without fly ash only developed to 24 MPa in the first 4 h hydration [11].

By adding fly ash into MPC will in turn contribute to the green environment. For MPC with fly ash, the physical property, chemical property, and durability have been investigated in the previous studies [12,13]. The previous research also considered that the cementing action was mainly attributed to the formation of struvite of potassium. In order to further understand the cementing mechanism, the morphology of reaction products and microstructure of cement are additionally analyzed. Both fine powder and grains of dead burned magnesia are used to prepare cement paste and bonding cluster samples, respectively. The reaction products and their micro-morphology in the two different test samples are examined by X-ray diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and optical microscopy, respectively.

2. Experiment

2.1. Raw materials

In the current study, the raw materials used are dead burned magnesia and monopotassium phosphate (MPP). The MPP is a chemical reagent in a form of a white grain crystal, which is manufactured by Guangzhou Reagent Factory (China). Two types of dead burned magnesia with the same chemical composition are used in the study. One is a fine magnesia powder (average particles size is 30.6 μm) and the other is magnesia grains (the particle size is 1 mm to 2 mm). Chemical composition of the dead burned magnesia is, MgO 89.51%, Al_2O_3 2.35%, SiO_2 4.91%, CaO 1.44% and Fe_2O_3 1.6% by weight. The chemical composition is determined by X-ray fluorescence spectrometry (XRF), and the particle size analysis is carried out by using a laser particle size distribution meter, model Counlter LS 230.

2.2. Test methods

2.2.1. Preparation and analysis of cement paste

The specimen of cement paste is made with fine magnesia powder, MPP and deionized water. The phosphate to magnesia ratio is 1:4, and water to dry binder ratio is 0.15. After the three ingredients were mixed, they hardened into the cement paste. Then the cement paste and its microstructure are analyzed by XRD (Philips PW1830), SEM (model JEOL-6300F), TEM (model JEM 2010), respectively.

2.2.2. Cementing and analysis of bonding magnesia grains

First, the saturated monopotassium phosphate (MPP) solution is prepared by solving MPP in deionize water. Second, magnesia grains are immersed into MPP solution in a small plastic bottle which is cured afterwards at a room ambient temperature. After several days, the bulk magnesia grains bond tightly together, becoming a cementing cluster. Then, the bonded magnesia cluster is taken out from the bottle, and is divided into two parts. One part is used for the study of the hydration products and microstructure of the bonded magnesia cluster. The specimen is prepared by the following procedure. The magnesia cluster is cast in epoxy in a plastic ring. After the epoxy hardened, it is polished by means of fine grinding in a progressive way. Then the specimen is coated with a carbon-palladium coating. The reaction products and microstructure are studied by optical microscopy (Olympus SZH10), XRD, SEM, respectively. To a long term observation, the other magnesia cluster part is put in a dry plastic bottle for 7 months, which allows air to go into the bottle, moisture in air can react continuously with the magnesia grains.

3. Result and discussion

3.1. Analysis of cement paste

3.1.1. Reaction products in the hardened cement paste

The XRD pattern of hardened cement paste is shown in Fig. 1(a). According to the diffraction peaks, there are two phases of crystal products were found in the XRD pattern, one phase is unreacted periclase. The dead-burned magnesia has a high intensity, which does not react completely during hydration. It may exist as a crystalline aggregate in hardened cement paste.

The other pahse is struvite of potassium, $MgKPO_4 \cdot 6H_2O$ (MKP) which is the newly produced mineral phase inside the cement paste. According to the JCPDS system, the JCPDS card number of MKP is 35-0812, and the characteristic peaks are $d = 4.241$ nm, 2.899 nm, 4.123 nm. At the same time, many diffused diffraction peaks exist around the main diffraction peaks of MKP. It can be inferred from the XRD analysis that the colloid species (or amorphous MKP) also appear in the hydration product. Regy and colleagues had shown that struvite exists not only as crystal form, but also exists as amorphous form, in their research work, phosphate recovery in waste water by crystallization [14].

The formation of amorphous struvite has a significant effect on the paste nature. Because the amorphous struvite

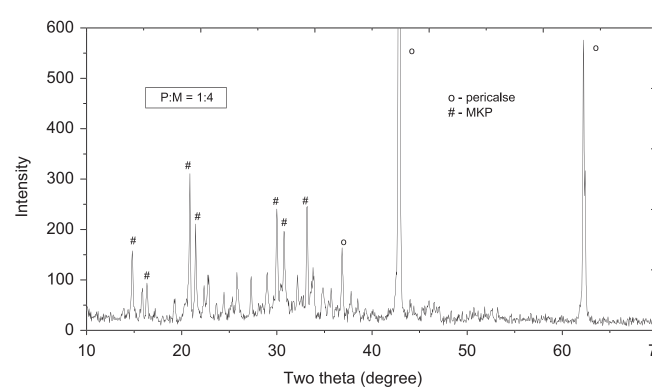

Fig. 1. XRD pattern of cement paste.