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Cementing mechanism of potassium phosphate based magnesium phosphate cement

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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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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

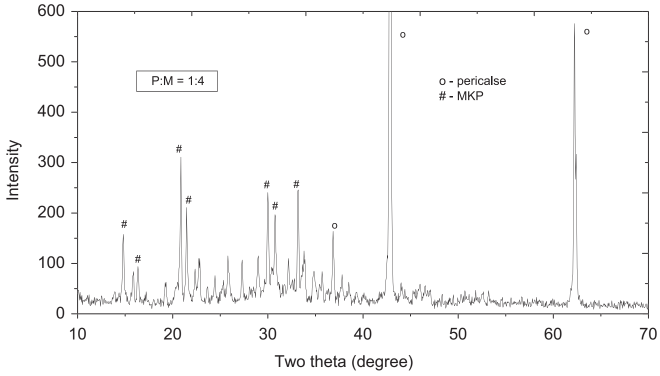

Fig. 1. XRD pattern of cement paste.

have a continuous structure and can fill the voids among the grains. As a result an uninterrupted microstructure is formed. The crystal products can constitute the framework which allows amorphous mass to fill in and cohere. Like the microstructure of he hardened Portland cement, both the amorphous species (mainly calcium silicate hydrate or C–S–H gel) and crystalline (mainly calcium hydroxide and ettringite) consist jointly of the microstructure, leading to the certain mechanical properties. In MPC, the coexisting of both crystal (periclase and struvite) and amorphous species contribute to the strength development by the similar way.

3.1.2. *SEM analysis*

Fig. 2 shows the SEM photos of cement paste after hydration for 1 h and 28 days. The microscopic photos indicate that short-bar-shape MKP products link each other, and the hardened cement paste has a tight join polycrystalline structure. The images show that the pattern of reaction products looks nearly the same after 1 h and 28 days, but the products are in a smaller size at 1 h. The growing of products may deliver a benefit effect on the strength development. Because as the hydration process continues, more reaction products are produced. Consequently a denser microstructure with a higher strength is obtained. This could explain the time-dependent mechanical properties of MPC system.

3.1.3. *TEM analysis*

Fig. 3 is the TEM electron diffraction photos of hardened paste. The TEM electron diffraction also indicates that hydration product of the MPC is a polycrystalline composite. The polycrystalline and amorphous species have different patterns under electron diffraction in the TEM analysis. Fig. 3(a) shows the result of MPC cement paste, where the polycrystalline diffraction rings are found by TEM-SAD analysis. Polycrystalline structure consists of many crystals joining each other on the boundaries. The electron diffraction pattern of polycrystalline is concentric rings [15]. On the other hand, the amorphous substance without a regular, ordered structure of crystalline solid shows diffuse halos as far as the diffraction pattern is concerned [16]. Fig. 3(b) demonstrates the diffuse halos on the basis of the electron diffraction analysis. Therefore, the results of XRD and TEM show both crystalline and amorphous MKP exist in the hydration products.

3.2. *Reaction products among the bonding magnesia grains*

3.2.1. *Observation of binding process*

After the magnesia grains are immersed into saturated MPP solution, the reaction starts from the grain surface, more reaction products formed around magnesia grains with time. Fig. 4 illustrates the micrographs of the magnesia grains

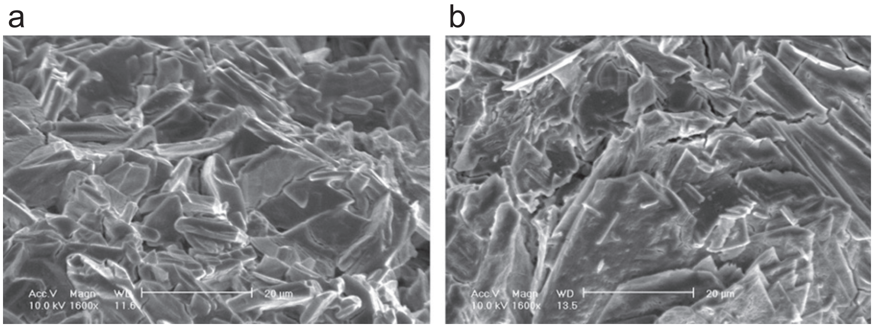

Fig. 2. Microscopic analysis of hardened cement paste: (a) hardened cement paste after 1 h, (b) hardened cement paste after 28 days.

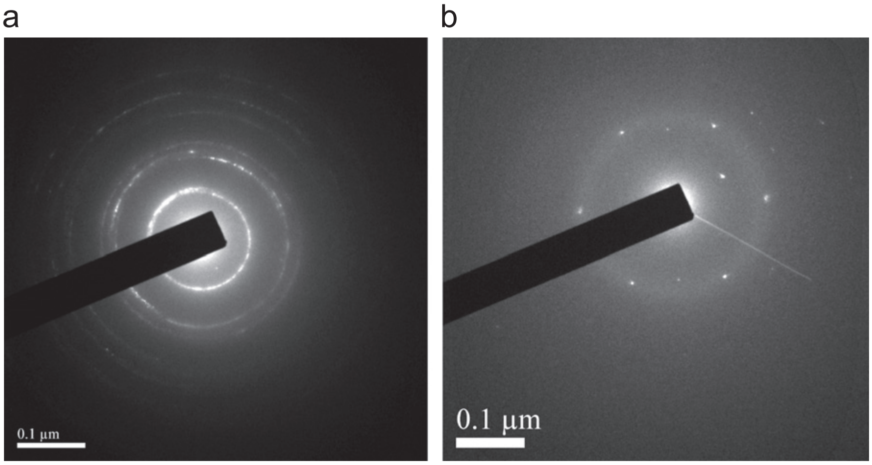

Fig. 3. TEM diffraction images of sample PM4: (a) polycrystalline ring pattern with inter-planar spacings, (b) crystal diffraction points and amorphous halo.

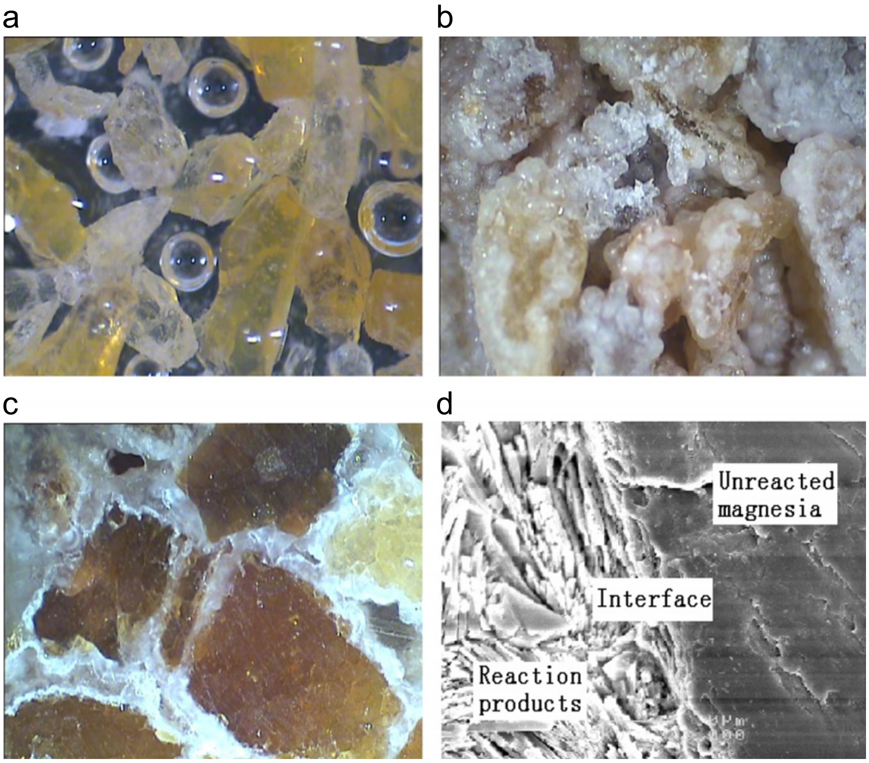

Fig. 4. Binding and products formation: (a) bubbles formed when reaction (20 ×), (b) white products on the grains (30 ×), (c) products around the grains (50 ×), (d) interface of products and magnesia.

before and after they bond together. The reaction between MPP solution and magnesia in the first minutes is observed with an optical microscopy. When the saturated MPP solution is dripped on the magnesia grains, some bubbles produced immediately (see Fig. 4(a)). But the bubbles cease to appear after about 3 min.

During immersing, magnesia is dissolved by MPP solution from surface. Struvite forms after the concentrations of magnesium, potassium (or ammonium) and phosphate ions exceed its solubility, leading to precipitation of struvite on the surface of magnesia grains. As is known, the precipitation of struvite, at a certain environment temperature, is mainly controlled by pH, supersaturation. An optimum pH for the precipitation of struvite exists, which is between 7 and 11 [15].

With immersion, hydration products accumulate more and more around magnesia grains, further bind the magnesia grains together to form a cluster. Fig. 4(b) shows that there is a layer of white reaction products developed on the surface of magnesia grains. The white reaction products are composed of fine particles. According to surface chemistry, these fine particles tend to cluster or to group together to form colloidal particles due to the reduction of the interfacial free energy (surface tension), which is attributed to the minimum surface area of sphere shape of fine particles. Observation from the direction of the bonded cross section, it is clearly demonstrated that the white products fill the voids among those magnesia grains and bond them together (see Fig. 4(c)).

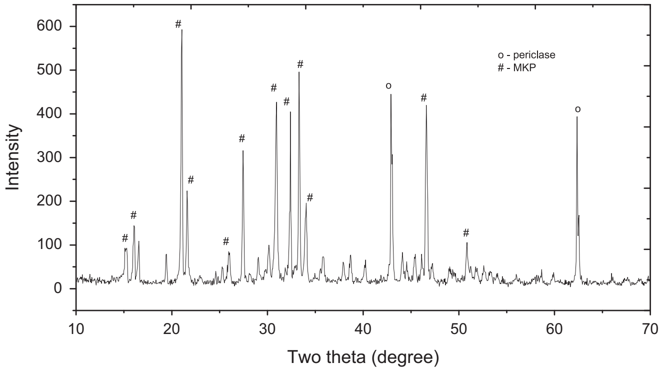

Fig. 5. XRD pattern of the bonded magnesia grains.

Fig. 4(d) shows the SEM image concerning the interface between hydration products and unreacted magnesia. In comparison with the unreacted pericalse, the newly formed structure is the amalgamation of rod-like products with voids.

According to the analysis, the binding effect is realized with the help of the white colloid orbicular products, which accumulate around the rim of the magnesia grains. These products fill the voids among grains and bind the grains together. If tiny magnesia grains with good particle size distribution are used, such as the fine magnesia powder, more reaction products will be produced, which will lead to a denser microstructure than by using large magnesia grains. Because of there are few voids in fine powder with good particle size distribution. The denser microstructure of cement paste will lead to a higher performance.

The XRD pattern of the bonded magnesia grain cluster is showed in Fig. 5. The crystalline phases in XRD patterns are unreacted magnesia and MKP. Diffusing peaks are

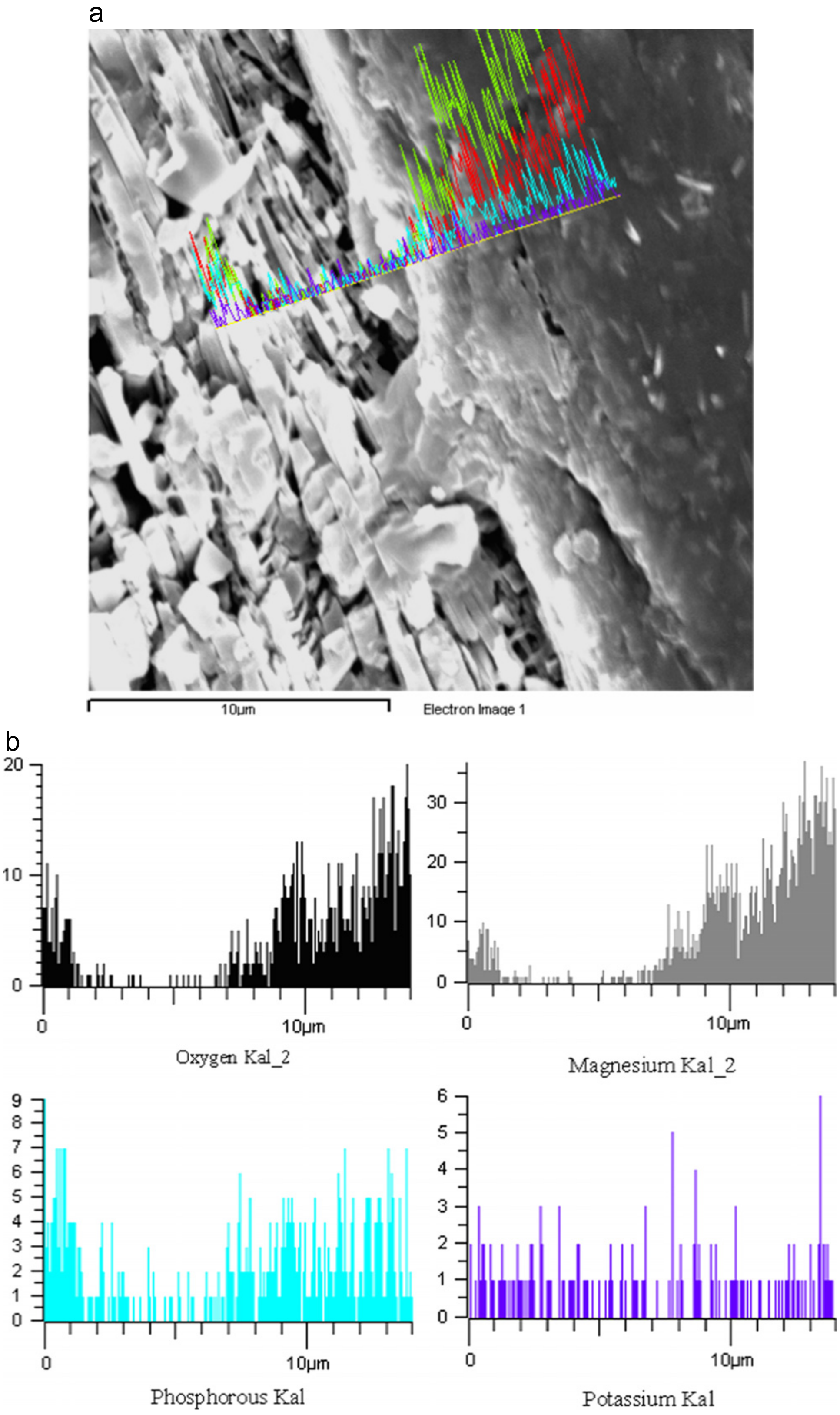

Fig. 6. SEM line scanning analysis of reaction interface: (a) interface of products and magnesia, (b) distribution of elements through the interface.

also found here. This indicates that amorphous stuff exists. By comparing Fig. 1 with Fig. 5, it is found that higher diffraction intensity of MKP presents in the bonded magnesia grain cluster. Because there is enough interparticle space among the magnesia grains, MKP crystals can develop more perfectly. However, inside the cement paste, the MKP crystals are much finer due to the dense microstructure. Therefore, the diffraction intensity of MKP is lower in the paste sample.

The reaction process can be stated as the following equations.

$$KH_2PO_4 \rightarrow K^+ + H_2PO_4^-$$

$$KH_2PO_4 \rightarrow K^+ + HPO_4^{2-} + H^+$$

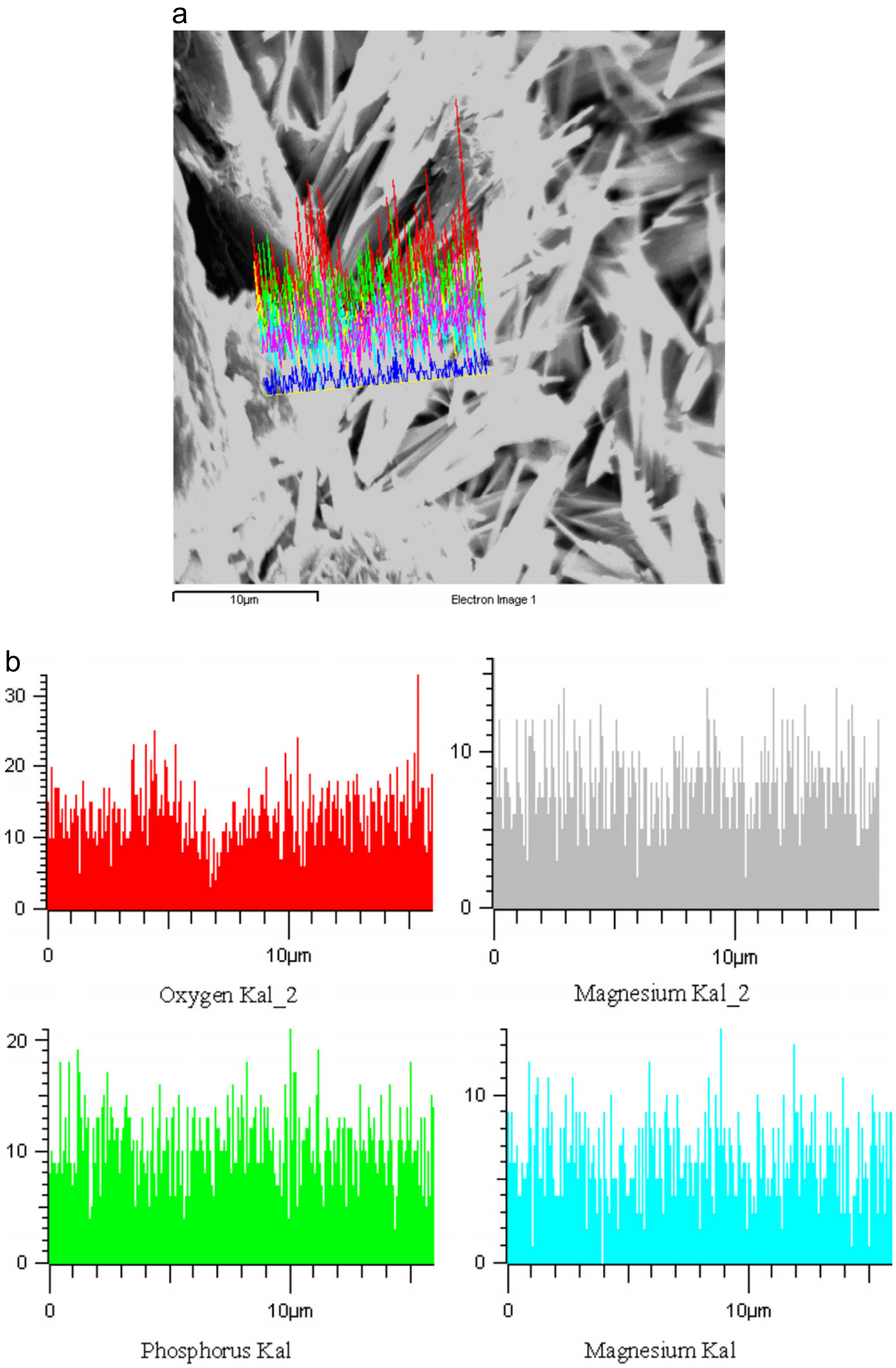

Fig. 7. SEM line scanning analysis of products: (a) electron image of reaction products, (b) elements distribution in the products.

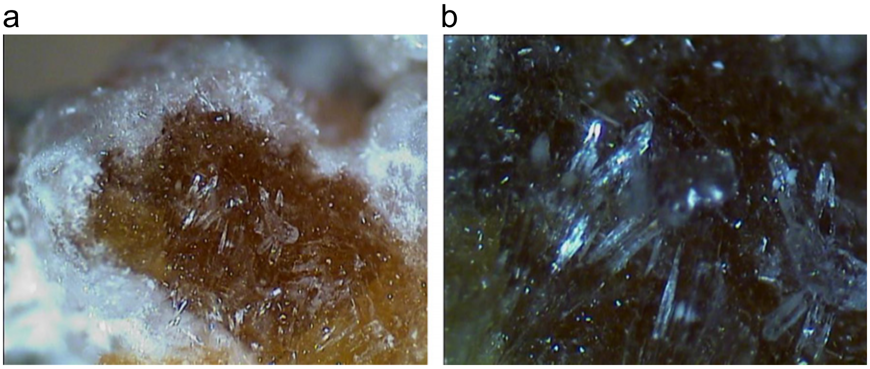

Fig. 8. Products formed on the grains surface after 70 days: (a) magnification of products (25 ×), (b) magnification of products (70 ×).

$$\mathrm{KH_2PO_4 \rightarrow K^+ + PO_4^{3-} + 2H^+}$$

$$\mathrm{MgO + H_2O \rightarrow MgOH^+ + OH^-}$$

$$\mathrm{MgOH^+ + 2H_2O \rightarrow Mg(OH)_2 + H_3O^+}$$

$$\mathrm{Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-}$$

$$\mathrm{Mg^{2+} + 6H_2O = Mg(H_2O)_6^{2+} K^+ + Mg(H_2O)_6^{2+} + PO_4^{3-} = MgKPO_4 \cdot 6H_2O\ (MKP)}$$

3.2.2. Observation of cementing interface of magnesia grain

Fig. 6(a) shows the electron image concerning the interface between hydration products and unreacted magnesia, and Fig. 6(b) illustrates the distribution of elements through the interface, which is analyzed by SEM-EDS line scanning. According the image, the rod-like products developed along the direction parallel to the surface of magnesia grains. The distribution of chemical elements in the interface shows that both element O and Mg have a similar distribution pattern. They have higher concentration in unreacted magnesia part, but lower concentration in the hydration product. Both element K and P have the similar intensity distribution in the reaction interface. The distribution intensity of Mg shows that its concentration is much lower in the hydration products than that in the unreacted magnesia part. It can be inferred that the microstructure of hydration product has a relative looser density than that of the unreacted magnesia part.

Fig. 7(a) shows a magnified image of reaction products inside the bonded magnesia grain cluster. The rod-like products orient in all directions and interlock each other. According to the SEM-EDS line-scanning analysis, the element distributions of Mg, P and K demonstrate a similar intensity, which means that these three elements have the similar atomic concentration in the hydration products. This rightly matches the atomic concentration ratio of the three elements in $\mathrm{MgKPO_4 \cdot 6H_2O}$ composition.

3.2.3. The long term observation of hydration products

In order to observe the bonding development among the magnesia grains, one part of the boned magnesia cluster was kept in the plastic bottle. After 70 days, the specimen is observed by means of optical microscopy. It is found that the MKP crystal on the surface of magnesia grain had been grown up (see Fig. 8) into a larger size. More hydrates present around the rim of magnesia grains, and some perfect MKP crystals developed on the surface of magnesia grains.

4. Conclusion

(1) According to XRD, SEM and TEM analysis, the current hardened MPC paste is polycrystalline which contains struvite and unreacted magnesia. Struvite has both crystalline and amorphous forms in the hardened paste. The residual magnesia acts as fine aggregate in the hardened microstructure. The coexisting of the two forms constitutes the hardened matrix, which is the performance basis of MPC system.

(2) According to microscope analysis, struvite forms from the magnesia surface at first, then develops to a layer around the unreacted magnesia grain. The struvite can link and interlock each other to form a continuum structure. When the magnesia grain sizes are tiny enough, the continuum structure can develop to a denser microstructure. Denser matrix structure can be obtained by using fine magnesia powder.

(3) According the 70 days observation, the MKP crystals develop to large size crystal in an open space. If the condition is allowable, struvite can form perfect crystal.

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