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Effect of Zn^{2+} on the early hydration behavior of potassium phosphate based magnesium phosphate cement

Zhenyu Lai [a,b,*], Xinchun Lai [b], Junbing Shi [a], Zhongyuan Lu [a]

[a] State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, PR China
[b] National Key Laboratory for Surface Physics and Chemistry, Mianyang, Sichuan 621907, PR China

HIGHLIGHTS

- Effect of Zn^{2+} on the early hydration behavior of magnesium phosphate cement are experimentally investigated.
- Higher Zn^{2+} concentration can prolong hydration process of magnesium phosphate cement.
- Zn^{2+} are mainly exited in hydration products.
- Leaching toxicity of zinc ions is lower than standard requirement.

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ABSTRACT

Magnesium phosphate cements (MPC) have potential applications in the solidification/stabilization of heavy metals. In this paper, the effect of Zn ions on the early hydration behavior of magnesium phosphate cement was investigated. The results showed that the physico-chemical characteristics of the MPC were significantly influenced by Zn ions. The addition of Zn ions increased the final setting time of the MPC and decreased the compressive strength of the MPC. The effect of Zn ions on the hydration characteristics of the MPC was examined by pH, heat of hydration, XRD, SEM and EDS. It is observed that the zinc ions have no effect on the phases of the hydration products of the MPC, but the crystalline degree of the product is influenced by the zinc ions. Furthermore, in the early hydration reaction process of magnesium phosphate cement, addition of Zn ions slows down the increasing of the pH and delays the hydration exothermic peak of the MPC. Most zinc ions are exited in hydration products. The result of the TCLP of the zinc ions showed that the leaching toxicity of the zinc ions is lower than the standard requirement.

1. Introduction

With the development of the chemical, mining, metallurgy and battery industries in China, large quantities of high-zinc waste have been discharged into the environment. Studies have shown that excessive intake of Zn will lead to toxic effects, such as chest distress, nausea and carcinogenesis [1].

Previous studies have shown that stabilization/solidification (S/S) processes of ordinary Portland cement (OPC) are effective as a means of disposing of most metallic waste streams. The cost of this process is lower than other methods. For OPC, the results of these processes are based on the hydration reaction of the cement. In the solidification process, its hydration product provides an interlocking framework to encapsulate the waste and this encapsulating can separate the waste streams from the environment [2]. However, Zn^{2+} has an effect on the hydration of OPC, the setting time of the OPC is prolonged and the compressive strength is reduced under the condition of high-zinc loading. These effects are harmful when disposing of the zinc waste with OPC [3]. On the other hand, magnesium phosphate cements (MPC) have potentially excellent performance in waste disposal, such as high early strength, good stability and low porosity [4–7].

Magnesium phosphate cements are also called chemically bonded phosphate ceramics. The raw materials of MPC usually include dead-burned magnesium, phosphate, and retarder. Ammonium dihydrogen phosphate ($NH_4H_2PO_4$, ADP) is the main phosphate used to prepare the MPC. Recently, most researchers have chosen potassium dihydrogen phosphate (KH_2PO_4, PDP) to prepare the MPC, as it does not release ammonia [8–10]. Moreover, Fan [11] found that mixing ADP and PDP can improve the strength of the MPC. MPC has been used as a structural material, especially

* Corresponding author at: State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, PR China.
E-mail address: laizhenyu@swust.edu.cn (Z. Lai).

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as a fast-setting repair material [12–17]. Many studies also show that magnesium phosphate cements can be applied for the stabilization/solidification (S/S) of low-level nuclear wastes and heavy metal wastes. In the process of stabilization/solidification of MPC, the metallic waste and nuclear waste can be reacted with phosphate, and with the effects of physical encapsulating, better performance of solidified forms can be achieved [18–22].

A review of the literature [23–25] on potassium magnesium phosphate indicates that the reaction product, struvite of potassium, is mainly formed by the following reaction:

$$MgO + KH_2PO_4 + 5H_2O = MgKPO_4 \cdot 6H_2O$$

This reaction is highly exothermic, and the heat of the reaction is released in a short time. After the hydration reaction, a lot of unreacted burned magnesium oxide remains in the MPC. Ding [21] found that in the early stage of the hydration process, crystalline and amorphous struvite of potassium forms at the magnesia surface, and the struvite will develop into a layer in a short time. Finally, unreacted dead-burned magnesium oxide is bonded strongly by struvite.

The most common retarder for MPC is borax. But borax also has a negative effect on the compressive strength. For the hydration process of MPC, the addition of borax delays and reduces the heat evolution, but the total heat is not affected [26]. The ratio of magnesium to phosphate (M/P) is also important to MPC. The literature [27,28] has shown that the properties of MPC such as compressive strength, setting time, and bonding strength are related to it. Moreover, Qiao [29,30] found that during the hydration process of MPC, there are earlier exothermic peaks, lower cumulative heat and a faster change rate of the pH with a higher M/P ratio.

As a type of fast setting cement, the early hydration process is very important for application of MPC. The aim of this paper is to investigate the effects of Zn ion content on the early hydration properties of MPC. The compressive strength, setting time, pH, and hydration heat were investigated. The phases and microstructure of samples were also measured. In addition, the leaching toxicity of Zn^{2+} was investigated by using the TCLP (Toxicity Characteristics Leaching Procedure) to determine the stability of Zn ions stabilized in the MPC. The results so far are promising for the application of MPC in stabilization/solidification of heavy metals.

2. Materials and methods

2.1. Materials

In this experiment, the starting materials include dead-burned magnesia (MgO), potassium dihydrogen phosphate, borax powder, zinc nitrate and water. The dead-burned magnesium oxide is supplied by Liaoning Xinrong Mining Group, China and its median diameter is 13 μm, the size distribution is given in Fig. 1. The chemical composition of the dead-burned magnesia was determined by X-ray fluorescence spectrometry (XRF) and the results are given in Table 1. The potassium dihydrogen phosphate and borax used in the current research were industry grade, and were provided by Fine Chemical Plant of Shifang, China. The zinc nitrate employed was an analytic grade chemical reagent which provided by Kelong chemical reagent factory, China.

2.2. Test methods

In order to investigate the effects of the zinc content on the setting time and compressive strength of MPC, all the sample mixtures prepared were divided into three series. These series are named as MP2, MP3 and MP4 respectively. For series MP2, the weight ratio of zinc nitrate to solid was controlled at values of 1%, 2%, 3% and 4%. Moreover, the weight ratio of dead-burned magnesia to potassium dihydrogen phosphate (M/P ratio) of series MP2 was 2:1, the weight ratio of the borax to dead-burned magnesia was 0.1 and the weight ratio of water to solid (w/s) was 0.14. Compared with series MP2, the M/P ratio of series MP3 and MP4 was changed to 3:1 and 4:1. Besides the M/P ratio, the other mixing proportions of series MP3 and MP4 were the same as for series MP2. The mixing proportions of all the samples are listed in Table 2.

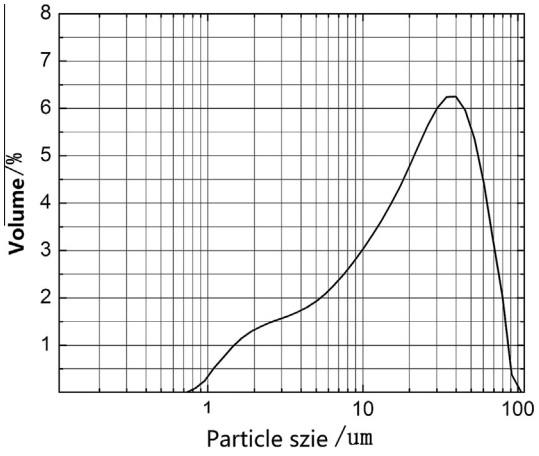

Fig. 1. Particle size distribution of dead-burned MgO.

For each sample, the setting time was determined using a modified Vicat needle. The setting time referred to the final setting time due to rapid hardening of the MPC. The slurry was cast in models of a 20 × 20 × 20 mm mould for measuring the compressive strength. All the samples were cured at room temperature of 20 ± 1 °C and relative humidity of 60. The compressive strength of the samples was tested at 12 h, 1 d, 3 d, and 7 d using universal mechanical tester (CMT5105, SANS, China) with a loading rate of 500 N S^{-1}.

The effect of Zn ion content on the pH during the reactions of the MPC was recorded by a PHS-3C acidimeter(INESA, Shanghai, China). For each sample, a total weight of 10 g of powder, including magnesia, PDP and zinc nitrate, was added into 100 mL of deionized water with moderate stirring at room temperature (Formula design of pH tesing see Table 3). The effect of Zn ion content on the heat of hydration of the MPC was monitored using a thermal activity monitor (TAM Air, TA Instruments, USA), the water to solid ratio of samples were controlled at 1:1, 2 g of powder including magnesia, PDP, borax and zinc nitrate were added into 2 mL of deionized water in tube, tube containing as prepared samples after moderate stirring were put into the instrument for hydration heat test (Formula design for heat of hydration testing see Table 4). The effect of Zn content on the hydration phases of MPC was analyzed by X-ray diffraction (PANalytical, X'Pert Pro, Netherlands). The diffraction data were collected by using Cu Kα radiation with a step of 0.03°/s, form 5° to 40°. The morphology and microstructure of the samples were observed by scanning electron microscopy (TM1000, Hitachi, Japan) and energy dispersive spectrometry (OCTANE SUPER, AMETEK, USA).

The leaching tests of Zn ions were conducted for 1d and 7d hydrated samples using the standard toxicity characteristics leaching procedure (TCLP) of EPA. The sample was ground to powder with a particle size less than 9.5 mm and leached in extracting solution (pH ≈ 4.93). 20 g of sample were added to 400 mL of extracting solution in a polyethylene bottle. The bottles were then vibrated for 18 h. After that, the leachates were filtered through a 0.45 μm membrane filter to remove suspended solids. The leached

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