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Investigation on early hydration features of magnesium potassium phosphate cementitious material with the electrodeless resistivity method

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ABSTRACT

An electrodeless resistivity method is applied to trace the early hydration behavior of magnesium potassium phosphate cement (MKPC). The relationship between setting times (including initial and final setting time) and the characteristic points of the electrodeless resistance is studied, aiming to establish a rapid testing method which could predict the setting time of MKPC. Moreover, a linear relationship between the standard compressive strength at 28 days and the resistivity at 24 h of MKPC is also established, and demonstrates that the resistivity and the standard compressive strength have a compact corresponding relationship. Therefore, the standard compressive strength of magnesium potassium phosphate cement could be predicted by electrodeless resistivity parameters.

1. Introduction

High temperature processing techniques, e.g., sintering, firing, melting and thermal shock, are very common in the field of traditional ceramics, while chemically bonded ceramics (CBCs), a terminology coined by Rustum Roy [1], are polycrystalline inorganic bodies or monoliths synthesized through chemical reactions instead of via heat treatment [2]. Magnesium potassium phosphate cement (MKPC) is a typical chemically bonded phosphate ceramic (CBPC) with excellent performance; CBPC is clinker-free, quick-setting, and has strong bonding strength and high early strength, volume stability, and deicer-scaling resistance [3–7]. The occurrence of MKPC is based on a through-solution chemical reaction (Eq. (1)) undergoing the dissolution of MgO and KH_2PO_4 to the crystallization of hexahydrate, $MgKPO_4{\cdot}6H_2O$ (Struvite-K) [8]. Theoretically, KH_2PO_4 (its solubility is 22.6 g, much higher than that of MgO (6.2 mg)) is first dissolved in water to create an acid environment where the magnesium ions can be extracted from MgO. The generation of magnesium ion is synchronized with the increase of pH environment due to the consumption of hydrogen ions. When the solution pH is approaching 6.0, crystal growth of struvite-K is initiated to form a cementing cluster, and arrives at the optimum at a pH value of about 9 [9]. According to the standard enthalpies of formation of the reactants and resultant (shown under Eq. (1)) [10], it is an exothermic reaction and the theoretical reaction heat is 124 kJ/mol when 1 mol KDP is completely reacted with magnesia.

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4{\cdot}6H_2O \quad (1)$$

Engineering-oriented studies on MKPC paste or mortar have attempted to obtain a high performance cementitious material by optimizing the formula of raw materials available [11]. Recently, some investigations were also moved to the reaction mechanisms of MKPCs [12]. However, as a rapid repair material, its setting time and early hydration process are critical in achieving a well-formed crystalline phase and a reasonable workability, because early mechanical strength of hardened MKPC paste are quantitatively related to the crystallinity of hexahydrate and the original capillary pores (namely, MKP-to-space ratio) [13].

Normally, the needle penetration method is conventionally employed to determine the setting time of cement paste, it is a method which need tester to conduct needle penetration measurement at a fixed interval, but manual operation tends to induce some errors because the interval is not a point of time, which will influence the control of setting time of building construction in engineering field, therefore viable alternative methods are needed [14]. In this study, a novel electrodeless resistivity measurement is applied to trace the early hydration procedure by electrodeless resistivity device (CCR-II), during to its high accuracy, automatic recording which replace the procedure of manual operation and explicit physical meaning greatly contribute to

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Table 1
Composition of MgO material.

Composition	MgO	Al_2O_3	Fe_2O_3	CaO	SiO_2	Other
Content (%)	90.42	2.39	1.39	1.51	3.16	1.13

investigate hydration process, the setting time and early strength of MKPC [15,16]. The characteristic points in the resistivity curve of MKPC paste with varying water-to-cement ratios can point out the setting times (e.g., initial and final setting time), which were confirmed by a Vicat setup (HG-80S penetration resistance meter) according to GB/T50080-2011. In addition, strong linear correlations were found between the compressive strength development and resistivity.

2. Materials and experiments

2.1. Experimental materials

The MKPC used for the experiment is composed of MgO (which is obtained from Fu-qin Trading Limited Company in Shanghai, China and dead-burned at 1500 °C), KH_2PO_4 (analytic reagent) and tap water, the proportion of MgO and KH_2PO_4 is 4:1, $Na_2B_4O_7{\cdot}10H_2O$ (analytic reagent) is a retarder used in this experiment and account for 4% of the quality of MgO. Table 1 presents the information about the composition of MgO material, and the X-ray diffraction analysis of the MgO powder which has been done is shown in Fig. 1.

2.2. Test procedure

In the experiment of electrodeless resistivity, MKPC paste of different water cement ratios was first grouted rapidly into an annular mold of the electrodeless resistivity device (CCR-II), and then a smooth surface of paste is acquired through vibration, so as to eliminate bubbles which are generated in mixing process. Finally, a plastic film is used to cover the mold, reducing evaporation. The recording system automatically samples with a threading interval of 5 s (sec), and resistivity is recorded for 1 day. The ambient temperature is maintained at 20 °C during the whole testing process. No-load resistance should be higher than 50000Ω to eliminate the influence of air resistance and the interference from electromagnetic fields in round space. After the testing process, a micrometer is employed to measure the average height of samples for data correction. The system for electrodeless resistivity measurement is shown in Fig. 2.

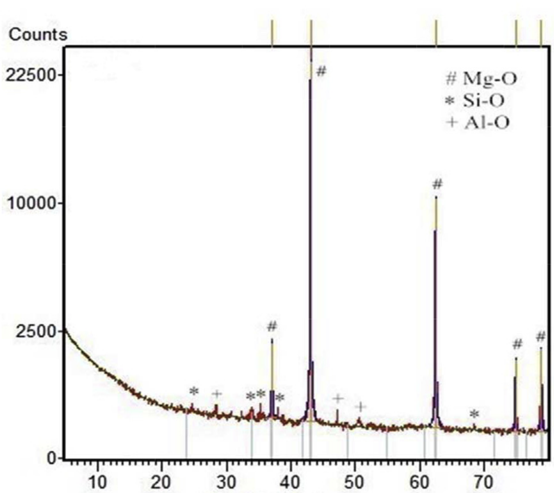

Fig. 1. X-ray diffraction analysis of MgO powder.

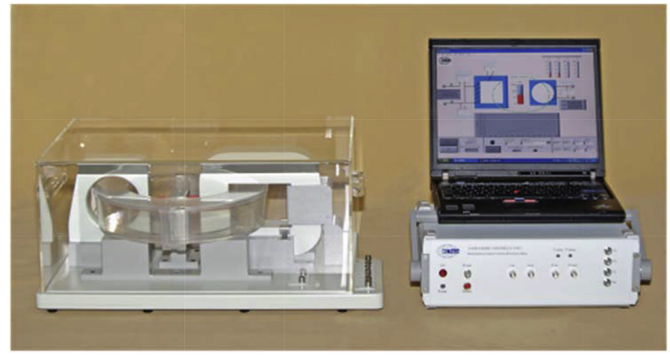

Fig. 2. The system for electrodeless resistivity measurement.

The initial and final setting times of cement were determined by the traditional method using a Vicat apparatus (HG-80S penetration resistance meter) according to GB/T50080-2002. Moreover, the cement cube axial compressive test (40 mm × 40 mm × 40 mm) was performed by YAW-300B microcomputer control electro-hydraulic cement pressure testing machine (made by Jianyi Instrument Machinery Limited Company in Wuxi, China) with test loading rate of (2400 ± 200) N/s until destruction, which are given by GBT 17671-1999 (ISO method). The samples are placed in a curing chamber (95 ± 5% RH, 20 ± 2 °C) until they are tested. The air content and porosity of samples at 28 days are measured and showed in Table 2.

X-ray diffraction phase qualitative analysis: samples were ground by an agate mortar until all sample powder went through a 325 mesh sieve; then began the X-ray diffraction test. Experimental conditions were as follows: Tube voltage (35 kV), Tube current (20 mA), Scanning (Continuous scan), Drive mode (θ-2θ Linkage), Scan speed (0.03°/s), Sampling time (1 s), Scanning angle range (5°-80°).

3. Results and analysis

As the hydration process of MKPC gradually evolves, hydration products are accumulated rapidly, and the ion concentration in liquid phase and the porosity of cement paste change continuously. Ion concentration in liquid phase affects liquid phase resistivity: generally the lower the ion concentration, the more liquid phase resistivity there is. Porosity also affects matrix resistivity: the smaller the porosity, the more matrix resistivity there is. Ion concentration and porosity cooperatively affect the resistivity of the cement paste system. Therefore, electrodeless resistivity method can be used to characterize the hydration process of cementitious material [17–23].

Electrodeless resistivity curves of different water cement ratio cement pastes of MKPC are drawn in Fig. 3. The resistivity curves all see a decrease in the beginning before rising gradually until the test is finished. The reason for this phenomenon is that the turbid liquid which is mixed by MKPC and the top water includes numerous ions, such as K^+, Na^+, Mg^{2+}, PO_4^{3-} and OH^- at an early stage. It has been demonstrated that the electrodeless resistance method is actually a test of ions' change. So the gradually increased ion concentration always accompanies the increase of electric current and the decrease of resistance until the resistivity curve reaches the lowest point, interior ion concentration goes to saturation, and the resistivity is minimal; by this time hydration products begin to take shape [24–26]. The sudden rise in the resistivity curves is due to the ion rapid dissolution in the previous stage

Table 2
Air content and porosity of samples at 28 days.

	0.25	0.3	0.35	0.4
Air content (%)	2.7	4.6	7.2	9.5
Porosity (%)	4.8	7.5	10.2	14.6