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Impacts of potassium permanganate ($KMnO_4$) catalyst on properties of hydrogen peroxide (H_2O_2) foamed porous cement slurry



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ABSTRACT

The foaming performance of porous cement slurry (PCS) foamed by H_2O_2 was greatly affected by types and dosages of catalysts. In this paper, KMnO₄ was adopted as catalyst to the H_2O_2 foamed PCS. The influences of the catalyst were investigated through the apparent density and coefficient of thermal conductivity (CTC) of each H_2O_2 foamed PCS under different water to cement ratios (w/c ratios). The catalyst's contribution degree to foaming effect (CDFE) in cement slurry was compared to the control group. The geometrical factors of pores in PCS were obtained through digital image processing technique. Morphology and components of PCS were analyzed with Scanning Electron Microscope and X-ray Diffraction, respectively. The results show that KMnO₄ can exert excellent catalytic effect in H_2O_2 foamed PCS. The Portland cement in PCS can hydrate as normal. KMnO₄ displays higher contribution degree to foaming effect for the slurry with higher w/c ratio. Therefore, increasing the amount of KMnO₄ catalyst under high w/c ratio is more helpful for the foaming effect than under low w/c ratio. The pores in cement slurry with KMnO₄ catalyst are more regular and the slurry with catalyst possesses higher porosity than the control group.

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1. Introduction

Due to their good heat insulation, sound absorption, and seismic resistance, porous cement based materials have been widely used in civil infrastructures for thermal insulation and noise absorption [1–3]. The behaviors of porous cement slurry (PCS) are fundamental to prepare porous cement based materials with satisfied properties. The chemical foaming agents and cement slurry are mixed together in PCS and air bubbles dissipate from the decomposition of chemical foaming agents and stay in the cement slurry. Currently, aluminum powder and H_2O_2 are two common chemical foaming agents used in porous cement based materials. However, air amount released from aluminum powder mainly relies on its reaction with alkaline materials in slurry [4], which makes the air releasing speed hard to control. On the other hand, the decomposition speed of H_2O_2 can be easily controlled by the amount of catalyst added to the cement slurry.

Recent studies on porous cement based materials mainly focus on factors such as water to cement ratio (w/c ratio), and foaming

* Corresponding author. E-mail address: zhouchangjun@hit.edu.cn (C. Zhou). agents [5–6]. For instance, Panesar et al. [7] tested three different foaming agents in cellular cement concrete, including a protein based agent and two synthetic agents. The results showed that foaming agent type had a significant effect on the captivity coefficient and thermal resistance of formed cement composites. Sanjayan et al. [8] studied the properties of lightweight geopolymer aerated by aluminum powder. Fly ash was substituted by aluminum powder with 5.0% of weight (wt%) in the specimens and the apparent density of the specimens was lowest. Nambiar et al. [9] found that when the water content was lower, the slurry mixture was too stiff, which makes pores break. However, when water content was high, the mixture was too thin to hold the pores, which then escaped from the mixture. However, the catalysts added to porous cement based materials have been rarely studied so far.

Currently, KMnO₄, FeCl₃, CuSO₄, etc. are used as catalysts for H_2O_2 . The mechanism can be interpreted from the view of energy [10]. The catalysts reduce activation energy to decompose H_2O_2 . In cement slurry, H_2O_2 molecule faces a complex environment, where water content, temperature and dynamic parameters of the released air are very unstable. Therefore, the pore size and amount in the cement slurry are also very unstable. Additionally, pore characteristics can influence thermal conductivity of foamed cement materials [11,12]. It is necessary to investigate the effects



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of catalysts on air dissipation and distribution in PCS. In this study, KMnO₄ chemical was added to cement slurry as the catalyst for H_2O_2 . The w/c ratio was varied as well. The apparent density and thermal conductivity of each type of PCS were tested to investigate the effects of the catalyst to the foaming effect of H₂O₂ in cement slurry.

2. Laboratory experiments

2.1. Raw materials

The ordinary Portland cement was used to cast all cement slurry in this study. The properties of this type of cement are shown in Table 1. 30 wt% H_2O_2 solution was adopted as foaming agent for the porous cement slurry, KMnO₄ chemical was planned to use as catalyst in PCS. Calcium stearate was used as foam stabilizer. Tap water was used for specimen preparation.

2.2. Specimen preparation

Cement slurry specimens with different mix design (see Table 2) were molded in laboratory. The dosages of KMnO₄ catalyst were 0.25%, 0.5% and 0.75% of the mass of H_2O_{21} , respectively. A mixer with paddles was used to mix PCS mixtures at room temperature. The mixing duration was 2 min. PCS preparation sequence is shown in Fig. 1. After mixing, specimens with a size of $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$ were casted into steel molds immediately. The specimens were cured in a curing chamber and demolded after 24 h and then cured in the chamber for 28 days. The temperature was kept at 20 ± 5 °C and the relative humidity was more than 90%. During the curing period, they were always covered with a plastic film.

2.3. Test methods

First, the specimens were dried in 40 °C and the mass and the size were measured. Each specimen was tested for three times and the averages were obtained. Then the volume and the apparent density of specimens were obtained. The CTC of cement slurry specimens was tested by a multifunctional rapid thermal conductivity tester according to the Thermal Insulation-Determination of Steady-State Thermal Resistance and Related Properties-Guarded Hot Plate Apparatus (GB10294-2008), a Chinese specification. Three duplicated samples of each group were prepared for the CTC test and the average testing results were calculated.

In order to study the pore characteristics in cement slurry, the cross-sections of specimens were pictured by digital camera and put into a commercial image processing software. The numbers and geometrical factors of pores in cement slurry, such as perimeter and area, were obtained from the commercial software. The porosity of the specimen was calculated by taking binarization deal and using black and white distribution ratio of the specimen image. Then, the shape factor (S) of the pores was calculated in Eq. (1). For the pores, the more S closer to 1, the more closer to the sphere. Otherwise, when S is greater than 1 and increases, the ellipsoid will be flatter. The shape factor can reflect the uniformity degree of pores in cement slurry [13]. Then number percentage of the pores with different shape factors was defined as the percentage of the number of pore with different shape factor to the number of total pores.

$$S = \frac{l^2}{4\pi A} \tag{1}$$

where, S – shape factor, no unit; l – perimeter of pore, pixel; A – area of pore, pixel × pixel.

The morphology of the milled PCS specimen was analyzed with S4800 Scanning Electron Microscope (SEM). The test was conducted in a vacuum. The SEM resolution was 3.5 nm and the test voltage was 3 kV.

The quantitative phase analysis of crystals in PCS after 28 d cured was conducted with X-ray Diffraction (XRD, D/MAX 2400 diffractometer, Cu-Ka radiation). In the test, filler milled from PCS specimens was scanned. The test voltage was 40 kV; the electric current was 100 mA and the XRD scan speed was $4^{\circ}/min$.





Fig. 1. Process of PCS preparation.

Table 2	
Mix design of cement slurry (g).

Cement	Water	Calcium stearate	H_2O_2	KMnO ₄
500	200	10	20	0.05 (0.1, 0.15)
500	225	10	20	0.05 (0.1, 0.15)
500	250	10	20	0.05 (0.1, 0.15)
500	275	10	20	0.05 (0.1, 0.15)
500	300	10	20	0.05 (0.1, 0.15)
500	200	10	20	-
500	225	10	20	-
500	250	10	20	-
500	275	10	20	-
500	300	10	20	-



Fig. 2. Apparent density of PCS without catalysts.

3. Results and discussion

3.1. Impact of w/c ratio on foaming effect

Five different w/c ratios were applied in cement slurry. In order to solely obtain the impact of w/c ratio on the foaming effect in cement slurry, no catalyst was used. The apparent density and

Fineness (80 μm Sieve residue)/%	Stability (boiling method)	Setting time/min		Compressive strength/MPa		Flexural strength/ MPa	
≦10	Qualified	Initial 201	Final 252	3 d 10.2	28 d 36.5	3 d 2.5	28 d 5.5

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