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Technical note

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, $KMnO_4$ 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 $KMnO_4$ can exert excellent catalytic effect in H_2O_2 foamed PCS. The Portland cement in PCS can hydrate as normal. $KMnO_4$ displays higher contribution degree to foaming effect for the slurry with higher w/c ratio. Therefore, increasing the amount of $KMnO_4$ 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 $KMnO_4$ catalyst are more regular and the slurry with catalyst possesses higher porosity than the control group.

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 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, $KMnO_4$, $FeCl_3$, $CuSO_4$, 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, $KMnO_4$ 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 H_2O_2 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. $KMnO_4$ 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 $KMnO_4$ catalyst were 0.25%, 0.5% and 0.75% of the mass of H_2O_2, 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 mm × 40 mm × 160 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-Kα 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°/min.

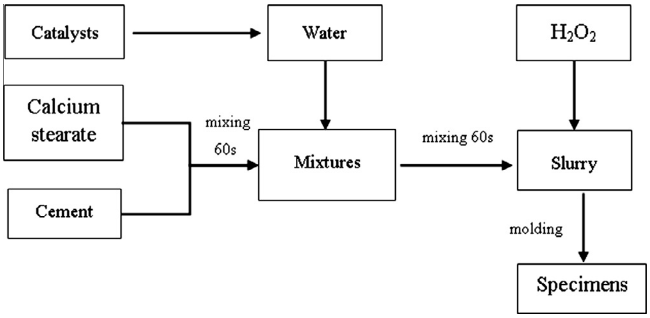

Fig. 1. Process of PCS preparation.

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	–

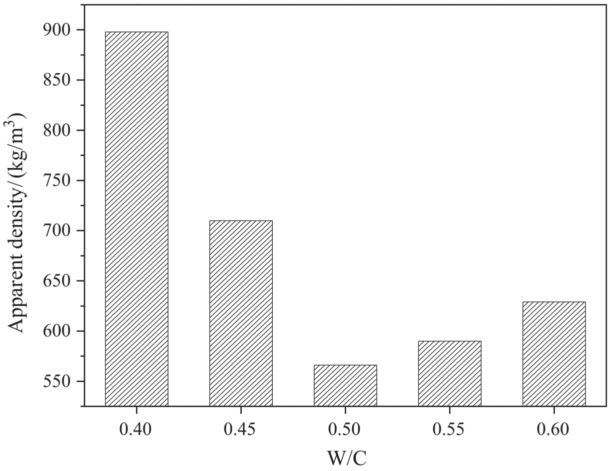

Fig. 2. Apparent density of PCS without catalysts.

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

Table 1
Properties of ordinary Portland cement.

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

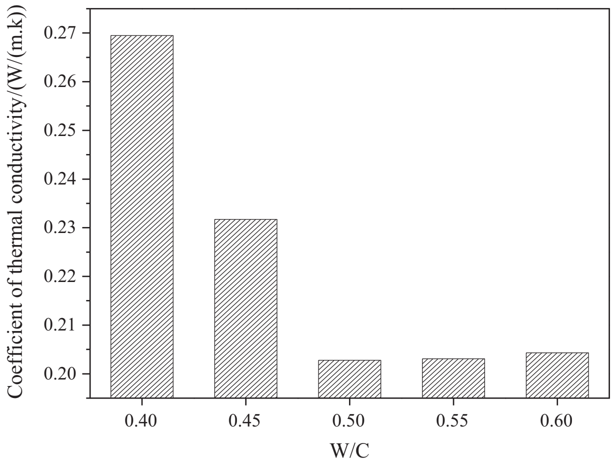

Fig. 3. The CTC of PCS without catalysts.

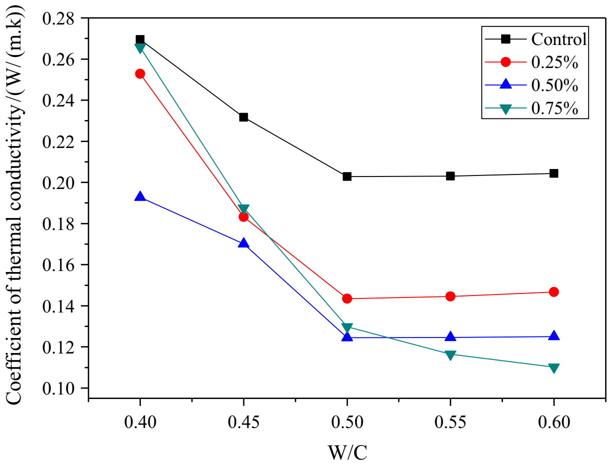

Fig. 5. The CTC of PCS with $KMnO_4$.

the CTC of cement slurry under different w/c ratios were tested and results are shown in Figs. 2 and 3, respectively. It can be seen that the apparent density and the CTC of cement slurry firstly decreased until w/c ratio of 0.5, then increased. It is believed that the decomposition of H_2O_2 ($2H_2O_2 = 2H_2O + O_2\uparrow$) is related to the w/c ratio and hydration heat of cement slurry. With a low w/c ratio, the hydration heat was dissipated slowly in cement slurry, delaying the decomposition speed of H_2O_2 [14]. Therefore, there will be still H_2O_2 not decomposed when cement slurry enters the sedimentation process. Additionally, a low w/c ratio makes the cement slurry condensed, so that pores are difficult to expand in cement slurry and pore size will be small. On the other hand, when the w/c ratio is over high, the cement slurry is easy to flow and bleeding occurs. In this case, pores can easily expand and move up to the surface and break [15]. The bleeding phenomenon also brings H_2O_2 up to the surface, which makes that part of H_2O_2 useless from the perspective of air-entraining because of the lower decomposition rate of H_2O_2 itself.

3.2. Impact of $KMnO_4$ on foaming effect

The cement slurry specimens with three different dosages of $KMnO_4$, i.e., 0.25%, 0.50%, and 0.75% weight of H_2O_2, were tested on their apparent density and the CTC. The results are shown in Figs. 4 and 5. It can be seen that the amount of $KMnO_4$ added to cement slurry influenced apparent density and thermal conductivity more under high w/c ratios than under low w/c ratios. That is to say, it is more effective for $KMnO_4$ as a catalyst to produce pores in PCS under a high w/c ratio in cement slurry.

Because the w/c ratio increases, the viscosity of the slurry is decreased, and the foaming resistance in cement slurry decreases. With $KMnO_4$, the pore formation rate of H_2O_2 is faster; and the density and the thermal conductivity of the slurry reduce. Therefore, the KMnO4 can exert catalytic effect better in the condition of high w/c ratio.

After adding amounts of H_2O_2 and $KMnO_4$, a large number of clusters of calcium silicate hydrate (C–S–H) and needle-like ettringite occurred in the PCS, as shown in Fig.6. In addition, The XRD pattern of the specimen as shown in Fig.7 reveals the presence of ettringite, portlandite, and other minerals, which indicates Portland cement in PCS can hydrate as normal.

3.3. $KMnO_4$' contribution degree to foaming effect

The catalyst's contribution degree to foaming effect (CDFE) in cement slurry is defined as the CTC percentage between the control group and the cement slurry with catalyst. The CDFE can be calculated by Eq. (2) and the results are shown in Fig. 8.

$$\mathrm{CDFE} = \frac{\mathrm{CTC}_{\mathrm{control}} - \mathrm{CTC}_{\mathrm{catalyst}}}{\mathrm{CTC}_{\mathrm{control}}} \times 100 \tag{2}$$

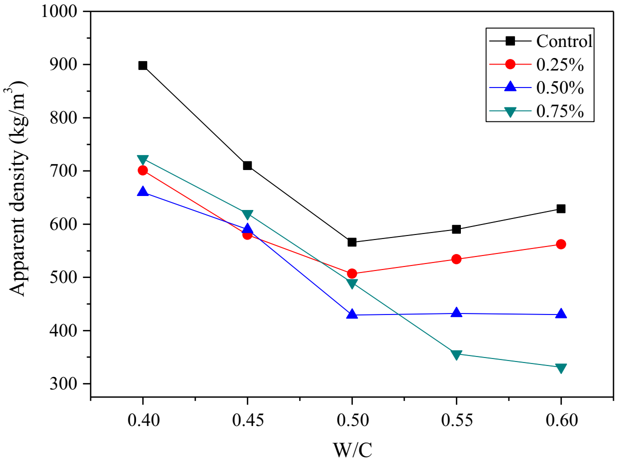

Fig. 4. Apparent density of PCS with $KMnO_4$.

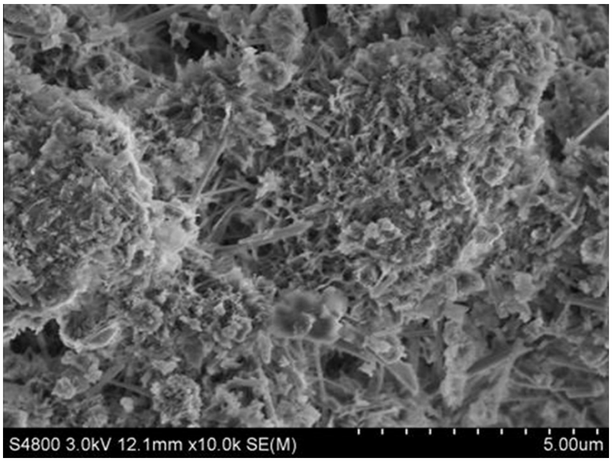

Fig. 6. SEM picture of the PCS.

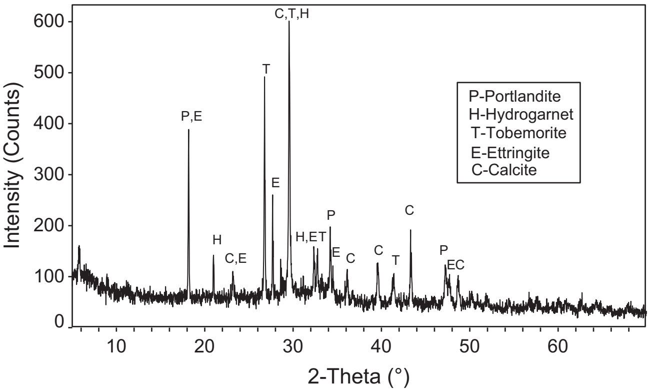

Fig. 7. XRD pattern of the PCS.

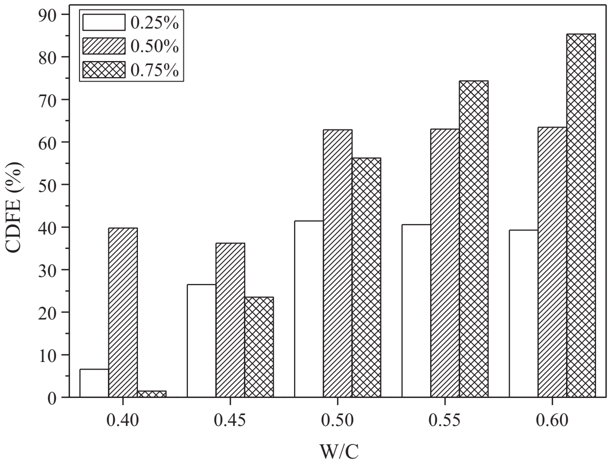

Fig. 8. The CDFE of the catalyst with different dosages.

For different dosages of $KMnO_4$, under low w/c ratio, the CDFE first increase and then decrease with the dosage increase of $KMnO_4$. When the w/c ratio is higher than 0.55, the CDFE evidently increases as the dosage of $KMnO_4$ increases.

The $KMnO_4$ and H_2O_2 dissociate in water as follows:

$$KMnO_4 = K^+ + MnO_4^-$$

$$H_2O_2 \rightleftharpoons HO_2^- + H^+$$

Since H_2O_2 is weak acid and MnO_4^- is unstable [16]. Therefore, $KMnO_4$ rapidly decomposes in the cement slurry under acid environment, that is:

$$4MnO_4^- + 4H^+ = 4MnO_2 \downarrow + 2H_2O + O_2 \uparrow$$

Meanwhile, H_2O_2 has the reducibility when meets strong oxidize. Therefore, the redox reaction takes place between H_2O_2 and $KMnO_4$ [17], as follows:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 \uparrow + 8H_2O$$

$$2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 \downarrow + 3O_2 \uparrow + 2OH^- + 2H_2O$$

Both H_2O_2 and $KMnO_4$ have the characteristics of strong oxidizing. H_2O_2 shows reducibility when meets $KMnO_4$ in the alkaline environment. The speed and efficiency of decomposition of H_2O_2 can be accelerated with the increase of $KMnO_4$. However, under a low w/c ratio, it takes H_2O_2 a long time to penetrate into the internal of the slurry. Then the high concentrated $KMnO_4$ on the surface of slurry makes H_2O_2 decomposing quickly, where the O_2 is rapidly produced. Additionally, in the condition of water shortage, the calcium stearates cannot arrange well around pores [18]. Therefore, the produced O_2 then quickly dissipates out from the cement slurry. That is the reason why a high concentrated $KMnO_4$ solution cannot make H_2O_2 to foam pores well in cement slurry with low w/c ratio.

3.4. Impact of $KMnO_4$ on pore characteristics

The w/c ratio for cement slurry specimens is 0.5 and the dosage of catalyst is 0.5%. The pictures for the three types of PCS are shown in Fig.9. The number percentages of shape factor of the pores in PCS are shown in Fig.10. It can be seen that the number percentages of shape factor of the pores are between 1.1 and 1.2 when the $KMnO_4$ is used for catalyst, indicating the pores regular. However, the number percentage is between 1.4 and 1.5 when there is no catalyst, indicating the pores in cement slurry irregular. It can be concluded that $KMnO_4$ with suitable dosage can exert better catalytic effect in cement slurry.

The pore characteristics, such as porosity, can also influence the CTC. Relation chart between CTC and porosity of the PCS with 0.50 w/c ratios and different catalyst dosages was shown in Fig.11. It shows that the porosity is increased after the addition of the catalyst. The porosity is roughly linear to the CTC. It indicates that the specimen with catalyst contains a large number of pores, in which

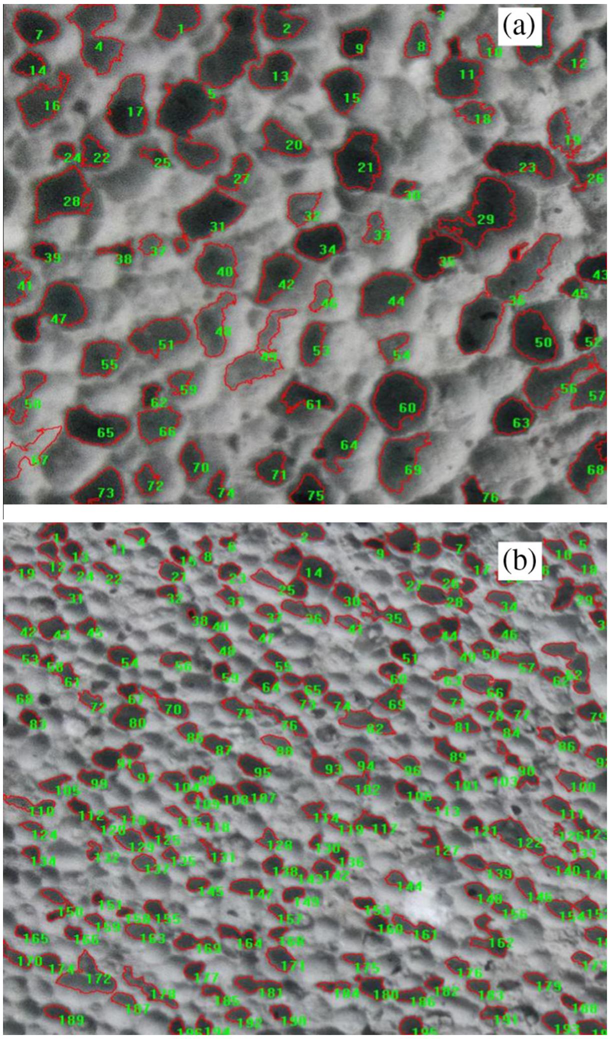

Fig. 9. Pore characteristics of PCS: (a) control group; (b) with 0.50% $KMnO_4$.

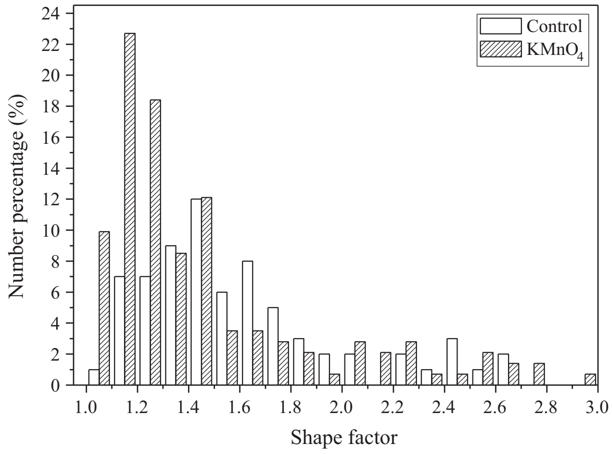

Fig. 10. The number percentages of the pores with different shape factors.

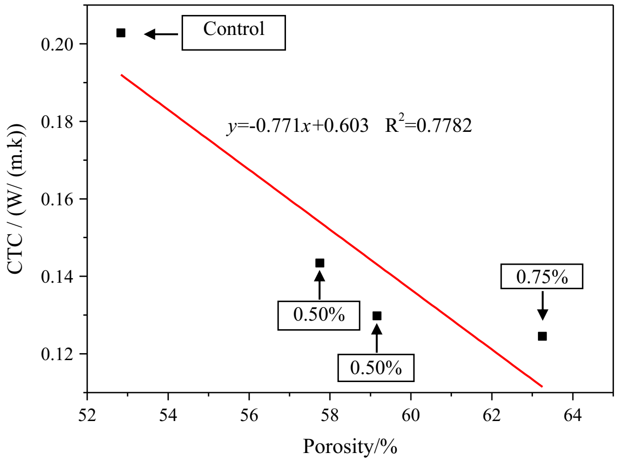

Fig. 11. Relation between CTC and porosity of PCS with different catalyst dosages.

the thermal conductivity of air or solution is much lower than that of the cement matrix. Therefore, The higher porosity, the lower thermal conductivity.

4. Conclusions

The foaming effect of H_2O_2 in cement slurry can be easily influenced by catalysts, including their types and dosages. In this paper, $KMnO_4$ catalyst was used in cement slurry. The influence of $KMnO_4$ on the foaming effect of H_2O_2 was compared with control group through apparent density, thermal conductivity, and pore characteristics analysis of cement slurry with different w/c ratios and catalyst dosages. Conclusions can be drawn as follows:

(a) The apparent density and thermal conductivity of cement slurry foamed by H_2O_2 were influenced by the w/c ratio of cement slurry. And they firstly decreased until w/c ratio of 0.5, then increased.
(b) When increasing the dosage of $KMnO_4$, the apparent density and thermal conductivity of cement slurry decrease under high w/c ratios while do not evidently decrease under low w/c ratios. A better catalytic effect can be achieved for $KMnO_4$ to the foaming effect of H_2O_2 in cement slurry under high w/c ratios rather than under low w/c ratios. In addition, Portland cement in PCS can hydrate as normal.
(c) Under low w/c ratio, the contribution degree to foaming effect decreases with the increase of $KMnO_4$ catalyst dosage. When the w/c ratio is higher than 0.55, the degree evidently increase with the increase of $KMnO_4$ dosage.
(d) The PCS with $KMnO_4$ catalyst contains more regular and more of amount pores than the control group. $KMnO_4$ chemical can exert excellent catalytic effect and increase the porosity in cement slurry foamed by H_2O_2. The higher porosity, the lower thermal conductivity.

5. Future researches

This is a preliminary study on the impacts of $KMnO_4$ catalyst on properties of H_2O_2 foamed PCS. The effects of both slurry microstructure and pore structure on strength of PCS and difference in pore structure with catalysts in combination will be studied in future.

Acknowledgements

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