Effect of Ultrasonication on the Thermal Insulation Performance of Porous Flyash-Based Ceramsite Cured for Different Durations

Zhizhou Zhou, Rongjun Pan*, Huiqin Wu, Yuhao Wu and Xin Wei

College of Civil Engineering, Guangxi University of Science & Technology, Liuzhou 545006, China
Email: rong_junpan@gxust.edu.cn

Abstract: Porous ceramsite has excellent thermal insulation performance due to numerous internal pores filled with gas which serves as a barrier to heat conduction. In order to control the pore structure of sintering-free porous ceramsite, the porous non-fired ceramsite with low thermal conductivity was prepared by ultrasonic irradiation. The effects of different natural curing time, ultrasonic irradiation time and power factors on the porosity of non-burning ceramsite were studied by measuring porosity, other physical properties, thermal conductivity and scanning electron microscopy. The results showed that: when the curing time was 6d, the ultrasonic processing power was 1944 W, and the ultrasonic time was 30min; The total porosity of ceramsite is 63.65%, the closed porosity is 12.77%, the thermal conductivity is 0.175 W/(m·K), and the thermal insulation effect is the best.

Keywords: Sintering-free porous ceramsite, ultrasonication, porosity, thermal insulation performance.

1. Introduction

The building energy consumption accounts for about 35% of total global energy consumption, about 60-70% of which was resulted from the poor thermal performance of the materials of building envelops [1]. As the heat transfer of building materials is mainly carried out by means of heat conduction [3-4], when porous thermal insulation materials are adopted in construction industry, not only the building energy consumption but also the yield of CO₂ can be reduced greatly [1-3]. Therefore, seeking building materials with desired thermal performance will be of greatly significance, providing a new orientation of energy saving and consumption reduction for construction industry [1-6].

Ceramsite is a kind of lightweight aggregate with excellent thermal insulation performance due to its numerous pores inside. When external walls are constructed with ceramsite concrete wall panels, about 30% building energy consumption could be reduced as it features excellent thermal insulation performance [2, 4, 5]. Moreover, when ceramsite concrete is used for the construction of high-rise and long-span architectures, the structure weight, foundation load, as well as construction cost can be reduced greatly [7]. The greatest challenge is to increase the porosity of the thermal insulation materials.

It has been demonstrated that ultrasonication can enhance the porosity via ultrasonic cavitation [6, 7]. When both soft coal and anthracitic coal are treated by using ultrasonic with various frequency, the...
porosity, including micropores, sub-micropores, mesopore, and macropores could be promoted, especially the sub-micropores [8]. With a fixed ultrasonic power, a dual-frequency mode would be superior to single frequency one in both the ultrasonic cavitation and the number of molecules of water vapor inside the cavitation bubbles [9]. Moreover, for the starch dispersed in water and ethanol, its porosity can be enhanced greatly [10]. However, unfortunately, rare research has been conducted to investigate the effect of ultrasonication on the porosity of flyash ceramsite to date. Therefore, in the present study, the effect of ultrasonication, including ultrasonication power [11], duration as well as the curing duration prior to ultrasonication, on the porosity of flyash ceramsite was investigated by using flyash, cement, quick lime, and calcined gypsum powder as raw materials. Moreover, the thermal insulation performance of the obtained flyash ceramsite was evaluated.

2. Experimental Section

2.1. Materials

The raw materials used for ceramsite preparation containing fly-ash, cement, calcined gypsum, and quick lime with a respective mass ratio of 25:5:2:1 were obtained from Ouweimu Machinery Manufacturing Co., Ltd. (Liuzhou, China), as shown in table 1. The components and proportion of flyash were determined according to the Methods for Chemical Analysis of Cement [21] and presented in table 2, in which Ignition loss rate is denoted as LOI. The particle diameter distribution of the raw mixture was determined by using a laser granulometer (LS13320, Beckman Coulter Co. Ltd.) and shown in figure 1, in which $d_{10}$, $d_{50}$, and $d_{90}$ were evaluated to be 1.847, 12.68, and 65.59 μm, respectively.

Table 1. Composition ratio of the raw mixture.

| Component | flyash | cement | calcined gypsum | quick lime |
|-----------|--------|--------|----------------|------------|
| Mass ratio| 25     | 5      | 2              | 1          |

Table 2. Chemical composition of flyash.

| Component | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | SO$_3$ | TiO$_2$ | K$_2$O | Na$_2$O | LOI |
|-----------|---------|-------------|-------------|-----|-----|--------|---------|-------|--------|-----|
| Proportion (wt.%) | 57.8 | 26.5 | 5.8 | 4.1 | 1.7 | 0.6 | 0.3 | 0.8 | 0.2 | 2.2 |

Figure 1. Particle diameter distribution of the raw mixture.
2.2. Preparation of Ceramsite

The used raw mixture and water for each preparation was determined to be 3.0 kg and 600.0 g according to our previous work [15]. The pelleting was performed on a ZL-500 disk granulating machine from Machinery Equipment Co. Ltd. (Zhengzhou, China), during which the water was sprayed to moisten the powder mixture homogenously. The pelleting process was conducted till spherical ceramsite with desired average diameter was achieved. The rotating angle and rotating speed were set to be 45° and 35 r/min by using a transmission, respectively.

Prior to ultrasonication, the obtained spherical ceramsite was naturally cured for different durations of 2, 4, and 6 days so as to evaluate the influence of curing duration on the porosity. The cured ceramsite was then exposed to ultrasonic irradiation by using an HL-2600 ultrasonic cleaner form Kepuda Electromechanical Equipment Co. Ltd. (Shenzhen, China). In order to investigate the effect of irradiation power and irradiation duration on the porosity of the ceramsite, various powers of the output 2160 W: 30%, 60%, and 90% and various durations of 10, 20, 30, and 40 minutes.

2.3. Pore Structure Characterization of the Obtained Ceramsite

As for thermal insulation performance, the total porosity may likely be the dominant factor. In the present work, therefore, the apparent porosity p was measured by the traditional drainage method on the basis of the Archimedes principle [22]. Prior to the measurement, the weighed ceramsite sample were vacuum dried in an oven at 100±5°C for 8 h till a constant weight, m1. The vacuum dried ceramsite was then immerged in water and heated to boiling for 2 h, followed by natural cooling to room temperature. The ceramsite was transferred into a measuring cylinder with certain volume of water and the variation of volume before and after the ceramsite was immerged into the water was denoted as V. The ceramsite was then collected and put onto a wringing towel to remove the water attached to the ceramsite, followed by the weighing of the ceramsite, which was denoted as m2. The apparent porosity, Papparent, could be evaluated according to Equation (1).

\[
P_{\text{apparent}} = \frac{(m_2 - m_1)}{V} \times 100\% \tag{1}
\]

The sample was then taken out and vacuum dried in an oven at 100±5 °C for 8 h, followed by grinding into powder. The powder was then transferred into a pycnometer containing certain volume of water whose mass was determined to be m3, followed by the determination of mass of the whole system, m4. The closed porosity, Pclosed, could be evaluated according to Equation 2:

\[
P_{\text{closed}} = \left[1 - P_{\text{apparent}} - \frac{(m_3 - m_1 - m_4)}{V} \right] \times 100\% \tag{2}
\]

The thermal conductivity of the obtained ceramsite was measured by using a TPS-1500 thermal constant conductivity analyzer (Hot Disk, Sweden). The microstructure of the cross-section of the ceramsite was characterized by using a S-3400N field-emission scanning electron microscopy (Hitachi, Japan).

3 Results and Discussion

3.1. Effects of Natural Curing Time, Ultrasonic Power and Time on the Porosity of Sintering-Free Porous Ceramsite

Figures 2 and 3 show the effect of ultrasonic time and power on the apparent and closed porosities of the ceramsite being naturally cured for 2 days and 4 days prior to ultrasonic treatment. It can be seen, for the samples being naturally cured for 2 d prior to ultrasonication, the apparent porosity increased from 30% to 49.68% with the ultrasonic time increases from 0 to 40 min; meanwhile, the closed porosity increased from 4.74% to 11.5%. For the samples being naturally cured for 4 d prior to ultrasonication treatment, the apparent and the closed porosity increased from 30% to 50.11% and 4.74% to 10.6%, respectively, with the ultrasonic time increases from 0 to 40 min. While the ceramsite was exposed to ultrasonic irradiation, the cavitation bubble in liquid will vibrate. Upon the ultrasonication, these cavitated bubbles will expand and generate cavitation bubbles, which will oscillate under further action [12]. It has been provided that ultrasonic irradiation can significantly
improve the connectivity between pores. Therefore, the both the open and closed porosity of the unburned ceramsite will increase under the effect of ultrasound [14]. However, the cavitation bubble vibration increases with the enhancement of ultrasonic power, and the kinetic energy of cavitation bubble vibration keeps in the stable cavitation state of expansion, contraction and oscillation within a certain frequency range, and there is the optimal excitation frequency of cavitation bubble steady-state vibration [13]. Moreover, it can be seen from figures 2 and 3 that when the ceramsite samples were exposed to three ultrasonic powers of 648, 1296, and 1944 W for increasing durations, both the open porosity and the closed porosity increase. However, with the duration surpassing 30 min, the closed porosity decreases apparently. During the ultrasonication, it could be observed that the longer the ultrasonication time, the more the broken ceramsite. Especially, when the ultrasonication time lasted over 30 min, some ceramsite would become broken and muddy, which result in decline of closed porosity and hence increase of open porosity. Therefore, the optimal ultrasonic treatment time could be determined to be 30 minutes.

![Figure 2](image1.png)

**Figure 2.** Effect of ultrasonic time and power on the apparent and closed porosities of the ceramsite naturally cured for 2 days prior to ultrasonic treatment.

![Figure 3](image2.png)

**Figure 3.** Effect of ultrasonic time and power on the apparent and closed porosities of the ceramsite naturally cured for 4 days prior to ultrasonic treatment.
Figure 4 shows the effect of ultrasonic time and power on the open and closed porosity of the ceramsite after being naturally cured for 6 days prior to ultrasonic treatment. It can be seen from the figure that the open porosity and closed porosity increased from 30% to 52% and 4.74% to 12.77%, respectively, with the ultrasonic time increasing from 0 to 4 min for the samples after being naturally cured for 6 d prior to ultrasonic treatment, which is also consistent with those being naturally cured for 2 and 4 days prior to ultrasonic treatment. However, in comparison with figures 2 and 3, both the open and closed porosity could be observed to increase slightly in figure 4. According to the previous work [15], the longer the curing time of unburned ceramsite is, the more complete the hydration reaction will be, resulting in higher cylinder compressive strength. However, a higher cylinder compressive strength will hinder the formation and expanding of pores, leading to less pores and small pore size, which in turn result in small porosity. Interestingly, a deviation presented that with the curing time increasing, an increasing trend of porosity was observed from Figure 2 to 4. This is because the measurement of the ceramsite was conducted 28 days later after the ultrasonic treatment. As for the sample cured only for 2 days, less strength was developed due to the less hydration. During the following storage, hydration would occur unavoidably, resulting in the shrinkage of pores because of the padding induced by the hydration products [16]. The shorter the curing time before ultrasonic treatment, the less the hydration reactions. After 2 days and 4 days curing, the porous ceramic particles with high porosity can be obtained by ultrasonic treatment. However, when the bubbles are large enough, they will collide with each other and expand to the other areas of the ceramic particles. In this process, once most of the bubbles break, they will collapse and form a solid again, and the pores will also be filled by hydration products. It is observed in the experiment that the strength of the ceramsite is very low due to the short time of natural curing [17]. After the ultrasonic treatment, a large number of broken ceramsite will be formed, and the small ceramsite will become slurry state, which is not conducive to the production of ceramsite [18]. However, the longer the curing time, the shorter the initial bubbles and holes, and the less the hydration reaction. Therefore, it is most appropriate to choose the ultrasonic treatment after 6 days of curing. It can be seen from Figure 2-4 that the ultrasonic power increases from 648 W to 1944 W, the porosity obviously increases with the increase of power [19]. Therefore, 1944 W is selected as the best ultrasonic power.

Figure 4. Effect of ultrasonic time and power on the open and closed porosity of ceramsite naturally cured for 6 days prior to ultrasonic treatment.

3.2. SEM Analysis
The promotion of porosity of ceramsite induced by ultrasonic treatment can exert great influence on the microstructure which governs the performances of ceramsite [20, 21].

When the ultrasonic duration was set to be 30 min, the samples cured for 2, 4, and 6 days prior to ultrasonic treatment were ultrasonicated at different powers of 648, 1296, and 1944 W, followed by
SEM measurement. As shown in Figure 5, with the increase of ultrasonic power from 648 to 1944 W, the number of open pores increases gradually; the amount of the closed pore for the sample cured for 6 days is larger than those for the samples cured for 2 and 4 days. Moreover, it can be observed that the hydration products and unreacted residues can be clearly seen. With regard to the former, they mainly include C-S-H cementitious material with poor hydrated calcium silicate and Ettringite with high crystal. C-S-H cementitious material can be divided into type I and type II, the former is fibrous, hairy, acicular and rod, the latter is honeycomb, network and cotton floccule [22]. It is obvious in the figure that the blank sample is dense. With the increase of ultrasonic power, it can be seen clearly that more honeycomb-like phases gather together in spherical shape, needle like and rod like hydration products, and some spherical materials with smooth surface, which should be unreacted fly ash [23]. When the ultrasonic power reaches 1944 W, abundant holes can be found in C-S-H gel, which indicates that when the ultrasonic power is too high, the cavitation effect is enhanced, the gap between the hydration products is increased, and more needle like hydration products are produced [24].

The samples cured for 6 days prior to ultrasonication were chosen as a probe to investigate the effect of ultrasonication time on the microstructure under the power of 1944 W. As illustrated in figure 6, when the sample was not exposed to ultrasonic irradiation, a few pores could be observed, which is formed by the accumulation of raw particles. With the increase of ultrasonication time, more pores and uniform pore structures could be seen, especially for the sample irradiated for 30 min. It can be seen from figure 5 that there are abundant honeycomb and rod like hydration products, which should be type I C-S-H gel and type II C-S-H gel. With the increase of time, the holes formed by rod crystal lapping gradually increase [25, 26], resulting in the uneven distribution of holes.

3.3. Effect of Ultrasonic Time and Power on the Bulk Density and Cylinder Compressive Strength of Ceramsite Naturally-Cured for 6 Days Prior to Ultrasonic Treatment

The effect of ultrasonic time and power on the bulk density and cylinder compressive strength of ceramsite naturally-cured for 6 days prior to ultrasonic treatment was conducted and shown in figures 7 and 8. It can be seen from the figures that as the ultrasonic irradiation time increases from 0 to 40 minutes, the bulk density and the cylinder pressure strength decrease from 835 to 670 kg/m³ and from 2.658 to 1.3 MPa, respectively. The compressive strength of ceramsite is mainly determined by its microstructure, including porosity, pore wall thickness, pore size and pore distribution. Reference [27] shows that the compressive strength of ceramsite is affected by the binder and porosity, and the main structure of porous materials is supported by the pore wall. As the amount of binder used in this experiment is the same, so it is only affected by the porosity. Combined with the porosity of the sample, longer ultrasonic irradiation time and higher power will lead to higher porosity. Therefore, the compressive strength of the cylinder will decrease as a function of ultrasonic irradiation time and power [28].

3.4. Effect of Ultrasonic Time and Power on the Thermal Conductivity of Ceramsite Naturally-Cured for Various Days prior to Ultrasonic Treatment

Figure 9-11 show the effect of ultrasonic time and power on the thermal conductivity of the ceramsite naturally-cured for 2, 4 and 6 days prior to ultrasonic treatment. It can be seen from the figures that when the samples were ultrasonicated at no matter 648, 1296 or 1944 W, the thermal conductivity would decline as a function of the ultrasonication time. Moreover, a higher ultrasonic power could result in relatively lower thermal conductivity. For example, when the samples naturally-cured for various days were irradiated under 1944 W, the thermal conductivity would decrease from 0.18 to 0.175 W/(m·K). According to literature [29, 30], the thermal conductivity of ceramsite is mainly predominated by the porosity, and the most effective way to reduce the thermal conductivity is to promote the porosity. In particular, the effect of closed porosity in ceramsite on thermal conductivity [31]. It can be seen from the figure that the change of thermal conductivity system of ceramsite sample corresponds to the change trend of porosity.
Figure 5. SEM images of the ceramsite cured for various times prior to ultrasonication ultrasonicated for 30 min under different ultrasonic power.
**Figure 6.** SEM images of ceramsite naturally-cured for 6 days ultrasonicated at 1944 W for different times.

**Figure 7.** Effect of ultrasonic time and power on the bulk density of ceramsite naturally-cured for 6 days prior to ultrasonic treatment.

**Figure 8.** Effect of ultrasonic time and power on the compressive strength of ceramsite naturally-cured for 6 days prior to ultrasonic treatment.
Conclusions
In this experiment, ultrasonic cavitation was used to enhance the porosity of ceramsite. The porous structure of ceramsite can be effectively obtained by using ultrasonic wave properly. After 6 days of natural curing, the ultrasonic treatment power is 1944 W, and the ultrasonic time is 30 minutes. The total porosity of ceramsite is 63.65%, and the closed porosity is 12.77%. The lowest thermal conductivity of the sintering-free porous ceramsite is 0.175 W/(m·K), and the effect of thermal insulation is the best.

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