Effect of MnO$_2$ and Li$_2$CO$_3$ on Compressive Strength and Thermal Conductivity of Aerated Concrete

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Abstract. This study aims to evaluate the effects of catalyst (MnO$_2$) and coagulant (Li$_2$CO$_3$) on the properties of aerated concrete consist of Portland cement, aluminate cement, and grade I fly ash by the chemical foaming method. In this experimental investigation, the compressive strength and thermal conductivity of aerated concrete were tested by more than 70 aerated concrete specimens with catalyst ranging from 0 to 2.0% and coagulant ranging from 0 to 4.0%. The results indicated that catalyst had a positive effect on the foaming efficiency when the foaming agent percentage is 4%. The positive impact reaches the peak when the catalyst percentage on 0.4%. Outcomes show that the compressive strength of aerated concrete decreases slowly with the increase of coagulant content. Still, the thermal conductivity decreases significantly due to the pore size of the foam increases. The study also reveals that the coagulant effect on ordinary Portland cement concrete setting is not apparent.

1. Introduction
In recent decades, with the implementation of China's building energy conservation policy, the research and application of green energy-saving building materials have been highly valued. As a green building material, aerated concrete is a lightweight composite material with many tiny and closed-cell pores. This composite material also includes other components, such as fly ash or silica fume, which is part of the traditional aggregate substitute to improve its mechanical properties [1]. Compared with ordinary concrete, lightweight, thermal insulation, and energy absorption are the advantages of aerated concrete [2], and especially low density aerated concrete [3] shows excellent performance in terms of fire resistance [4], sound insulation [5], and workability [6]. Nowadays, as an increasingly important role in engineering construction, aerated concrete is expected to replace the use of organic building materials in the construction industry (e.g., the structural shock absorption, the insulated wall panels, the mine backfilling, and antiknock protection) [7,8]. Simultaneously, many products (such as non-structural parts, building partitions, sandwich plate cores, road substrates, energy-absorbing or cushioning systems, etc.) made of aerated concretes are used in engineering construction widely [9].

Unlike foamed concrete produced by the physically foaming method, aerated concrete is prepared utilizing the chemically foaming method, which involves a complex chemical reaction between the foaming agent and concrete slurry. The chemical reaction generates a large amount of gas inside the slurry to form many small and uniform pores in the concrete. In terms of the production process and performance control, aerated concrete is more complicated than the foamed concrete. Some scholars
have made contributions to the research of aerated concrete. Gu et al. [10] used aluminum powder as an expansion agent to compare the performance of autoclaved aerated concrete with the foamed concrete, and concluded that the aerated concrete is more economical in waste utilization. Liu et al. [11] prepared the aerated concrete with different water-binder ratios and hydrogen peroxide content by chemical foaming method, tested and compared its frost resistance and stomatal characteristics. They concluded that foam concrete's frost resistance could be improved by avoiding excessive water-binder ratio, increasing the number of pores with a cross-sectional area of less than 0.05mm², and making foam with a proper pore size grading. Jiang et al. [12] studied the relationship between the pore structure and the macroscopic performance of aerated concrete. They concluded that the proportion of pores with a bubble pore diameter within 100 μm is positively correlated with the concrete strength. Wu et al. [13] obtained the relationship between the compressive strength and pore characteristics of hydrogen peroxide foamed concrete by studying the hardening accelerator’s influence on the early performance of lightweight composite foamed concrete. Liu et al. [14] found that the compressive strength increase as the maximum roundness decreases under the same porosity of foamed concrete by investigating the relationship between the compressive strength and pores’ characteristics through image analysis. It is well known that adding the catalyst to aerated concrete can effectively improve the foaming efficiency, but there are few studies on the influence of coagulant and catalyst on the strength and thermal conductivity of aerated concrete.

In this paper, ordinary Portland cement and aluminate cement was selected as the primary materials to prepare the aerated concrete, and the effects of catalyst and coagulant on the strength and thermal conductivity of aerated concrete were studied. The relationship between the two admixtures and the physical properties of aerated concrete was analyzed by comparing the experimental results.

2. Experimental program

2.1. Materials and pieces of equipment

The materials used in the experiments are P.O.42.5 Portland cement (produced by Jidong Cement Co., Ltd), CA50-II aluminate cement (produced by Zhengzhou Kanghui Co., Ltd), Level-I fly ash (produced by Shanxi Hejin Longjiang fly ash plant). A few properties of these two types of cement are reported in Table 1. The foaming agent used in the experiments herein is hydrogen peroxide(H₂O₂), the catalyst is manganese dioxide (MnO₂), the coagulant is lithium carbonate(Li₂CO₃), the water reducer used is polycarboxylate superplasticizer, and the water is plain tap water.

The equipment used in the test included a mixer (produced by Zhejiang Shaoxing Shunda Instrument Factory, 30L volume, 48r/min), drying oven (produced by Guangzhou Baihui Instrument, working temperature range from 10℃~300℃), WES-600 hydraulic servo universal testing machine (produced by Shanghai Xieqiang Instrument), DRCD-3030B double-plate thermal conductivity tester (produced by Beijing Zhongke Road Construction Instrument), CX-12000 small scale (500g/0.01g, for weighing additives), ALH electronic scale (30kg/0.1g, for weighing water, cement, fly ash), constant temperature and humidity concrete curing room.

| Cement type       | Specific surface area / (m²/kg) | Cement setting time /min | SiO₂ / % | Al₂O₃ / % | Fe₂O₃ / % | Flexural strength /MPa | Compressive strength /MPa |
|-------------------|--------------------------------|--------------------------|----------|-----------|-----------|------------------------|---------------------------|
| Portland cement   | 300                            | 170                      | 210      | 20.0      | 5.0       | 2.0                    | 5(3d)                      | 30(3d)                    | 52(28d)                   |
| Aluminate cement  | 347                            | 120                      | 246      | 8.3       | 50.8      | 2.2                    | 6.5(1d)                    | 7.6(3d)                   | 55.7(1d)                  | 65.7(3d)                  |

2.2. Mix design

The first experiment consists of five series. In Table 2 the mix design of each series of specimens analyzed in this study is reported. The ratio of Portland cement and aluminate cement is 2:1. The content of MnO₂ is 0, 0.5%, 1.0%, 1.5%, and 2.0%, respectively, based on the total mass of cement, fly ash, and water. Each series consists of six aerated concrete cube specimens.
Table 2. Mix design of the tested specimens of aerated concrete with MnO\(_2\) content as variable

| Series No | Portland cement/g | Aluminate cement/g | Fly ash/g | Water/g | Calcium stearate | H\(_2\)O\(_2\) | Li\(_2\)CO\(_3\) | MnO\(_2\) | Polycarboxylate superplasticizer | Water cement ratio |
|-----------|-------------------|-------------------|-----------|---------|-----------------|-------------|-------------|---------|-------------------------------|------------------|
| 1#        | 3200              | 1600              | 1200      | 2100    | 2.0%            | 4.0%        | 2.0%        | 0       | 1.0%                          | 0.35             |
| 2#        | 3200              | 1600              | 1200      | 2100    | 2.0%            | 4.0%        | 2.0%        | 0.5%    | 1.0%                          | 0.35             |
| 3#        | 3200              | 1600              | 1200      | 2100    | 2.0%            | 4.0%        | 2.0%        | 1.0%    | 1.0%                          | 0.35             |
| 4#        | 3200              | 1600              | 1200      | 2100    | 2.0%            | 4.0%        | 2.0%        | 1.0%    | 1.0%                          | 0.35             |
| 5#        | 3200              | 1600              | 1200      | 2100    | 2.0%            | 4.0%        | 2.0%        | 2.0%    | 1.0%                          | 0.35             |

The second experiment consists of five series. In Table 3 the mix design of each series of specimens analyzed in this study is reported. The content of Li\(_2\)CO\(_3\) is 0, 1.0%, 2.0%, 3.0%, and 4.0%, respectively, based on the total mass of cement, fly ash, and water. Each series consists of six aerated concrete cube specimens and two plate specimens. (a series of the same mix ratio without aluminate cement is set as the control series for each series).

Table 3. Mix design of the tested specimens of aerated concrete with Li\(_2\)CO\(_3\) content as variable

| Series No | Portland cement/g | Aluminate cement/g | Fly ash/g | Water/g | Calcium stearate | H\(_2\)O\(_2\) | Li\(_2\)CO\(_3\) | Polycarboxylate superplasticizer | Water cement ratio |
|-----------|-------------------|-------------------|-----------|---------|-----------------|-------------|-------------|-------------------------------|------------------|
| 6#        | 8000              | 4000              | 3000      | 5250    | 2.0%            | 4.0%        | 0.4%        | 0                              | 1.0%             | 0.35             |
| 7#        | 8000              | 4000              | 3000      | 5250    | 2.0%            | 4.0%        | 0.4%        | 1.0%                          | 1.0%             | 0.35             |
| 8#        | 8000              | 4000              | 3000      | 5250    | 2.0%            | 4.0%        | 0.4%        | 2.0%                          | 2.0%             | 0.35             |
| 9#        | 8000              | 4000              | 3000      | 5250    | 2.0%            | 4.0%        | 0.4%        | 3.0%                          | 3.0%             | 0.35             |
| 10#       | 8000              | 4000              | 3000      | 5250    | 2.0%            | 4.0%        | 0.4%        | 4.0%                          | 4.0%             | 0.35             |

2.3. Specimen preparation, curing condition and testing conditions

In line with most of the relevant literature's experimental tests [15], the aerated concrete specimens were prepared in three steps. Firstly, according to the mix design, dry cement mixture was produced by mixing cement, fly ash, catalyst, foam stabilizer, accelerator, and superplasticizer for 20 seconds using a high-intensity mixer to prevent aggregation of fine materials. Then, add tap water into the mixer and stir with the dry cement mixture for 120 seconds to obtain an evenly-blended cement slurry. In the second stage, add the foaming agent to the mixer, mix it quickly for 10 seconds, and then pour the uniform concrete slurry into the mold. In the third stage, scrape the mold’s surface after the initial setting, cover the concrete under laboratory environmental conditions, keep the surface moist, and then demold after 24 hours. The specimens are cured in the standard curing box, and the distance between the specimens is 10–20mm. The specimen's surface should be kept moist and avoid exposure to rushing water. For each series of tested samples reported in Table 3 and Table 4, two different curing time are analyzed, as illustrated in Figure 5 and Figure 6. In particular, for each series half specimens were cured in the room at temperature (20±2 °C) and moisture characterized by the relative humidity of 95% for 3 days; the other half were cured at the same conditions for 28 days.

This experiment focuses on the compressive strength and thermal conductivity of aerated concrete. According to Ref. [16], the aerated concrete's compressive strength is characterized by the 100mm*100mm*100mm cube specimens, and the thermal conductivity is characterized by the 300mm*300mm*30mm plate specimens. Before the compressive strength test and the thermal conductivity test, the specimens were put in the drying oven and kept at 60 °C and 80 °C for 24 hours respectively, and then dried to the constant weight at 100 °C. The constant weight standard is characterized by the difference in the same test specimen's weight at 4-hour intervals of not more than 0.2%. Measure the mass in the dry state and calculate the dry density after taken out the test specimens from the drying oven according to Ref. [17].
Figure 1. Cube specimens and details of surface

Figure 2. Unconfined uniaxial compression test

Note: There are six specimens in each series, the first three are cured for 3 days, and the other three are cured for 28 days

The WES-600 hydraulic servo universal testing machine is used for the unconfined uniaxial compressive strength test. Put the test specimen in the lower steel plate's center before starting, adjust the spherical bearing under the lower steel plate when the upper steel plate is close to the test specimen, make the upper steel plate and the upper surface of the specimen contact evenly. Apply the load continuously at the speed of 2kN/s until the test cube specimen is damaged.

Figure 3. Specimens: (a) test plate, (b) outer crack of the cube specimen, (c) internal crack of the cube specimen

Figure 4. The pore structure of specimens: (a) specimen surface (b) 8-order grayscale image, (c) Binary graph
3. Results and discussion
The compressive strength of specimens is calculated according to equation (1)

\[ f_{cc} = \frac{P}{A} \]  

Where \( f_{cc} \) is compressive strength (MPa); \( P \) is the load (N); \( A \) is the area of the specimen (mm²).

Table 4. Compressive strength and dry density of aerated concrete with different MnO₂ content

| Series No | MnO₂ (%) | Cs(3d) (MPa) | Cs(28d) (MPa) | ACs(3d) (MPa) | ACs(28d) (MPa) | ADd (kg/m³) |
|-----------|----------|-------------|--------------|--------------|----------------|-------------|
| 1#        | 0        | 1.99        | 1.97         | 1.92         | 3.44           | 3.48        |
| 2#        | 0.5      | 1.88        | 1.94         | 1.89         | 3.35           | 3.32        |
| 3#        | 1.0      | 1.67        | 1.66         | 1.66         | 3.00           | 2.97        |
| 4#        | 1.5      | 1.39        | 1.39         | 1.39         | 2.58           | 2.73        |
| 5#        | 2.0      | 1.52        | 1.50         | 1.51         | 2.45           | 2.45        |

Table 5. Compressive strength and dry density of aerated concrete with different Li₂CO₃ content

| Series No | Li₂CO₃ (%) | Cs(3d) (MPa) | Cs(28d) (MPa) | ACs(3d) (MPa) | ACs(28d) (MPa) | ADd (kg/m³) |
|-----------|------------|-------------|--------------|--------------|----------------|-------------|
| 6#        | 0          | 1.88        | 1.86         | 1.93         | 3.12           | 3.10        |
| 7#        | 1.0        | 1.80        | 1.72         | 1.73         | 3.03           | 2.99        |
| 8#        | 2.0        | 1.67        | 1.66         | 1.71         | 2.87           | 2.88        |
| 9#        | 3.0        | 1.42        | 1.40         | 1.41         | 2.81           | 2.78        |
| 10#       | 4.0        | 1.34        | 1.36         | 1.30         | 2.67           | 2.63        |

Tables 4 and 5 show the test results of the aerated concrete's compressive strength and dry density under different catalyst and coagulant contents, respectively. There are six specimens in each series, and No. 1-1 represents the first one in the first series. Take the first three specimens of each series to measure its 3-day compressive strength (Cs), and calculate the average compressive strength (ACs). Take the last three specimens of each series to measure its 28-day compressive strength and calculate the average compressive strength. Measure and calculate the average dry density (ADd) of each series of test specimens.

A general overview of the effect of admixture on compressive strength and dry density of aerated concrete is shown in Figures 5 and 6. It can be seen from Figure 5 that the first series specimens' dry density and compressive strength are the highest among the five series. The dry density and compressive strength of aerated concrete decreased significantly with the content of MnO₂ increases in the range of 0~1.5%. When the content of MnO₂ is 1.5%, the dry density and compressive strength (3d) of aerated concrete are the valley values, of which the dry density is 375.2kg/m³, which is 29.4% lower than the average value of the first series. The compressive strength (3d) is 1.39 MPa, which is 29.1% lower than the average value of the first series. It can be seen that MnO₂ can effectively reduce the dry density of the aerated concrete. The H₂O₂ fully completes the foaming process when the MnO₂ content is 1.5% under the premise that the H₂O₂ content is 4.0%.
The variation trend of uniaxial compressive strength and average dry density with Li$_2$CO$_3$ content is analyzed, as shown in Figure 6. It can be seen from Figure 6 that changing the Li$_2$CO$_3$ content has the most significant influence on the average dry density of aerated concrete, which decreases significantly with the increase of Li$_2$CO$_3$. The decrease of average dry density is due to the increase of porosity as it can shorten the initial setting time of aerated concrete. Figure 6 also shows that when Li$_2$CO$_3$ content is less than 4%, the foaming rate of H$_2$O$_2$ is higher than the initial setting rate of the aerated concrete. Compared with Figure 5 and Figure 6, it can be found that the foaming rate of H$_2$O$_2$ is too fast at the beginning due to the presence of MnO$_2$ when Li$_2$CO$_3$ content is 0, part of the gas generated by the chemical reaction escapes into the air. After the beginning, the foaming rate of H$_2$O$_2$ gradually decreases; thus, the generated gas is trapped inside the concrete structure. In other words, the number of pores in concrete depends on the bubbles produced by H$_2$O$_2$ during the initial setting period of concrete. Although MnO$_2$ can accelerate the foaming rate of H$_2$O$_2$, the foaming rate also decrease obviously over time, and the addition of Li$_2$CO$_3$ can make the aerated concrete enter the initial setting process when the foaming rate of H$_2$O$_2$ is highest. Therefore, by changing the content of MnO$_2$ and Li$_2$CO$_3$, the foaming process and setting process in the aerated concrete can be balanced, and the aerated concrete with better performance can be obtained.

The Thermal conductivity of the test plate, according to equation (2)

$$\lambda = \frac{W \cdot \delta}{2(t_R - t_L) \cdot A} \times 10^3$$  \hspace{1cm} (2)

Where $\lambda$ is the thermal conductivity ($w/(m \cdot K)$); W is the power of the central heater (w); A is the thermal area (300x300mm$^2$); $\delta$ is the thickness of test plate (30mm); $t_R$ is the temperature of the hot side of the test plate (°C); $t_L$ is the temperature of the cold side of the test plate (°C).

Table 6 shows the test results of the thermal conductivity and dry density of aerated concrete with different coagulant content. The thermal conductivity is abbreviated to Tc; the average thermal conductivity is abbreviated to ATc; the dry density is abbreviated to Dd; the average dry density is abbreviated to ADd, and the names of the control series without aluminate cement are abbreviated to Tc', ATc', Dd' and ADd'.

| Serial No. | Li$_2$CO$_3$ (%) | Tc (W/ (m K)) | ATc (W/ (m K)) | ADd (kg/m$^3$) | Tc' (W/ (m K)) | ATc' (W/ (m K)) | ADd' (kg/m$^3$) |
|------------|-----------------|--------------|---------------|----------------|--------------|---------------|----------------|
| 6#         | 0               | 0.32         | 0.33          | 0.36           | 388.3        | 0.28          | 0.28           | 413.6          |
| 7#         | 1.0             | 0.34         | 0.38          | 0.36           | 390.8        | 0.33          | 0.31           | 380.5          |
| 8#         | 2.0             | 0.36         | 0.36          | 0.36           | 392.9        | 0.37          | 0.36           | 362.4          |
| 9#         | 3.0             | 0.38         | 0.37          | 0.38           | 401.6        | 0.36          | 0.38           | 304.5          |
| 10#        | 4.0             | 0.37         | 0.36          | 0.37           | 396.0        | 0.42          | 0.42           | 276.7          |

Figure 7. Effect of Li$_2$CO$_3$ content on the Tc and Dd of plate specimens

Figure 8. Effect of Li$_2$CO$_3$ content on the Tc' and Dd' of plate specimens in the reference series
Figure 7 shows the change cures of the plate specimens' compressive strength and thermal conductivity under the different coagulant content. In the second experiment, since used the same aerated concrete slurry used in each series, therefore the influence of Li$_2$CO$_3$ on the dry density of aerated concrete was not analyzed in the second experiment (it has been analyzed in Figure 6). As was discussed about coagulant content and shown in Figure 7, the plates' ATc of each series decreases with the Li$_2$CO$_3$ increase when the MnO$_2$ content is 0.4%, which is also because the Li$_2$CO$_3$ can shorten the initial setting time of aerated concrete. MnO$_2$ leads to a high foaming rate of aerated concrete at the initial stage; many bubbles were produced and trapped in the aerated concrete structure, thus reducing the test plates' thermal conductivity. Figure 8 shows that with increasing coagulant Dd' and Tc' of the test plates in the comparison series have little change; it is interesting to find that Li$_2$CO$_3$ has no apparent effect on the solidification of Portland cement in the complete experiment.

4. Conclusions
In this work, an experimental campaign comprising 70 aerated concrete specimens has been conducted to investigate the effect of catalyst and coagulant on the development of thermal conductivity and compressive strength. It has been found that with the increase of MnO$_2$, the test specimen's dry density decreases gradually and tends to be stable on the 0.4% MnO$_2$ and 4% H$_2$O$_2$. The concrete's 3d and 28d compressive strength also stopped falling when the MnO$_2$ content was 0.4% and finally became stable. The difference here observed is that adding the MnO$_2$ can significantly improve the foaming efficiency and reduce the aerated concrete's dry density. When the content of MnO$_2$ reaches 0.4%, the foaming rate of H$_2$O$_2$ reaches the peak value. For the composite of Portland cement and Aluminate cement, Li$_2$CO$_3$ can make the cement slurry setting shorter than the bubble stability. Thus the bubble can stably be stored in the cement slurry to avoid fracture or fusion. But the density, compressive strength(28d), and thermal conductivity of the test specimens have little change with the increase of Li$_2$CO$_3$ through analysis control series without Aluminate cement.

The following conclusions can be drawn according to the test results: (1) when the H$_2$O$_2$ content is 4%, the addition of the MnO$_2$ can improve the effectiveness of the H$_2$O$_2$ significantly, and the effect is maximized when the MnO$_2$ is 0.4%. (2) Li$_2$CO$_3$ has no apparent effect on the coagulation of Portland cement. But for the composite of Portland cement and Aluminate cement, With the increase of Li$_2$CO$_3$ content, the aperture of the bubbles inside the test specimen increased, the thermal conductivity decreased significantly, the compressive strength remained unchanged. The next thing to be studied is the influence of aerated concrete's moisture content on the compressive strength and how to increase its compressive strength under the premise of reducing the thermal conductivity. This study is only part of the overall research plan due to the too long period for producing and preparing aerated concrete. The subsequent comparative analysis of the test results will be conducted from a micro perspective.

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