

Article

Experimental Study on Mechanical and Thermal Properties of Backfill Body with Paraffin Added

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Abstract: Based on phase-change heat storage backfill, paraffin microcapsules were selected as the phase change material and were directly mixed with backfill materials for preparing backfill specimens. The mechanical and thermal properties of specimens with different paraffin percentages and slurry concentrations were tested and analyzed. The results show that compressive strength gradually decreases with an increasing paraffin percentage while it significantly increases with increasing slurry concentration, thermal conductivity decreases with increasing paraffin percentage and specific heat capacity increases with an increasing paraffin percentage and slurry concentration. For a paraffin percentage from 0% to 10%, compressive strength decreases by an average of 22.5%, thermal conductivity decreases by an average of 43.8% and specific heat capacity increases by an average of 8.7% at a phase-change temperature of 30 °C. For a slurry concentration from 68% to 72%, compressive strength increases by an average of 4.12 times, and specific heat capacity increases by an average of 3.5% at a phase-change temperature of 30 °C. The weakening effect of phase-change materials on compressive strength can be effectively improved by the increase of slurry concentration, and the increases of paraffin percentage and slurry concentration can both improve the sensible heat storage capacity of backfill materials.



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Keywords: heat storage; paraffin microcapsules; backfill specimens; compressive strength; thermal properties

1. Introduction

With the gradual decrease and exhaustion of shallow mineral resources, deep mining has become an inevitable trend; about 90% of the mines in China are facing deep mining at present. The safety problems caused by high ground stress and the thermal hazards caused by high geothermal temperature have gradually become the important factors restricting the effective mining of deep deposits. Given these problems, based on the idea of the collaborative exploitation of mineral resources and geothermal energy [1], the concept of phase-change heat storage backfill is proposed, taking solid wastes in mines mixed with cementing agents as basic backfill materials, and a certain dosage of phase-change material (PCM) is added into the backfill body. PCM relies on the physical phenomenon of absorbing or releasing a large amount of latent heat during the material phase transition to store and release energy. In this study, the accumulation and storage of geothermal energy are achieved through melting phase-change materials. During the heat harvesting process, phase-change materials release heat to the heating fluid through solidification. This makes the backfill body meet the requirements of mechanical properties for controlling ground pressure, supporting surrounding rock, and preventing the caving of surrounding rock

and ground subsidence, and meeting the requirements of thermal properties for gathering, storing and extracting geothermal energy.

The mechanical properties of backfill body, as a key structure for supporting surrounding rock, have always been the research focus of backfill mining technology. Numerous researchers have conducted comprehensive studies on various aspects of the mechanical properties of backfill bodies that incorporate solid wastes [2–8]. However, to realize the exploitation of geothermal energy while backfill mining, the study of the thermal properties of the backfill body is also an important aspect. Some researchers have tested and analyzed the mechanical and thermal properties of concretes. Zhang X [9] analyzed the effect of the amount of paraffin added as PCM on the thermal and mechanical properties of the filling material. The results showed that the addition of paraffin resulted in the loss of backfill soil structure, and decreased thermal conductivity, density and compressive strength, but effectively improved the thermal properties of the filling material, such as specific heat capacity and heat storage capacity. Other scholars have prepared composite phase-change materials using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ /expanded vermiculite [10], paraffin (PA)/expanded graphite (EG) [11] and decanoic acid/lauric acid [12], and have reached similar conclusions.

In building construction, it is common to incorporate PCMs into building walls to enhance the heat storage performance of the envelope structure. By adding PCMs to the walls, the ability of the building to store and release heat effectively is improved, contributing to better thermal comfort and energy efficiency [13–18]. The investigation of the mechanical and thermal properties of concrete materials containing PCMs is a significant focus in the field of building energy conservation. Researchers actively explore the incorporation of PCMs into concrete to assess their impact on mechanical strength, thermal conductivity, specific heat capacity, and other relevant properties. This research aims to develop concrete materials that not only provide structural integrity but also possess enhanced thermal storage and insulation capabilities, contributing to improved energy efficiency and building sustainability. Alsaadawi et al. [19] conducted experiments on the use of post-pyrolysis carbon obtained from waste tires for PCM in cement mortar to evaluate the effect of different PCM ratios on the thermal properties of concrete. The results show that composite materials have both strength performance and additional energy storage functions [20]. According to the phase transition of materials during the phase transition process, phase-change materials can be divided into four types: solid–solid, solid–liquid, solid–gas and liquid–gas. Due to the significant difference between the diameter and spacing of gas molecules compared to liquids or solids, phase-change materials with gas phases often have a large rate of volume change, leading to poor system stability. Therefore, solid–liquid phase-change materials have undoubtedly become a research hotspot, with research mainly focusing on inorganic, alcohol, fatty acid and paraffin materials. The thermal energy storage of inorganic hydrated salt PCM has attracted much attention due to its obvious advantages such as high energy storage density, non-toxicity and economy [21]. Lian P et al. [22] have prepared a modified PCM with low undercooling and stable form, using disodium hydrogen phosphate dodecahydrate as the matrix and sodium thiosulfate pentahydrate as the nucleating agent. Fatty acids have a high latent heat of phase transition, and Ong et al. [23] studied the extraction of coffee oil from waste coffee grounds as PCM. Analysis shows that coffee oil contains about 60% to 80% fatty acids, with a phase transition temperature of about 4.5 ± 0.72 °C and a latent heat value of 51.15 ± 1.46 J/g, indicating good thermal stability. The literature [24] introduces a composite PCM made by impregnating rice husk ash with lauryl alcohol and adding it to concrete. The results show that the composite PCM undergoes a melting phase transition at 19.97 °C, and its latent heat storage capacity is 99.60 J/g. Sobolciak et al. [25] reported on the thermal performance of PCM based on linear low-density polyethylene, paraffin and expanded graphite. Research has shown that PCM with a higher paraffin content exhibits better latent heat capacity. In the literature [26], PCMs for buildings composed of an acrylonitrile–styrene–acrylate copolymer, polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene triblock copolymer and paraffin were fabricated by melt blending. The results indicate that adding paraffin can achieve

an excellent cooling and heating performance (both up to 15 °C). Xie et al. [27] prepared paraffin wax/high-density polyethylene (HDPE)/expandable graphite (EG) composite phase-change materials. The introduction of EG can significantly improve the heat transfer rate of PCM. By optimizing the proportion of each component, sample PCM10-5 (HDPE 10 wt%, EG 5 wt%) was prepared. However, it is worth noting that paraffin will completely leak at 70 °C. According to Chen's research [28], almost all polymers/PCM made from paraffin will leak. To solve this problem, Wang et al. [29] prepared and studied a new type of hollow ceramsite (HC) compounded with paraffin, added it to a structural functional lightweight aggregate concrete (LWAC) and studied the mechanical and thermal properties of LWAC using HC paraffin. Wang et al. [30] studied the influence of the addition of encapsulated phase-change materials on the thermal properties of cement-based materials. The results show that the encapsulated phase-change material increases the phase-change enthalpy of cement-based composites, but decreases its thermal conductivity. In the study conducted by Gbekou et al. [31], the researchers studied the effects of microencapsulated MPCM on the mechanical properties (such as compressive strength, bending strength, etc.) and thermophysical properties (including thermal conductivity and heat capacity, etc.) of cement mortar. The results show that adding 8 wt% MPCM into cement mortar produces an ideal combination of improved mechanical strength and enhanced thermal performance.

In the context of phase-change heat storage backfill, the backfill materials encompass a range of components, including solid wastes, cementing agents, additive agents, and PCMs. The backfill body, designed to store heat, is created by solidifying backfill slurry with varying compositions and proportions. Consequently, its mechanical and thermal properties diverge from those of traditional backfill used in mining and the concrete materials commonly employed in building envelopes. At present, there are few studies on the mechanical and thermal properties of the backfill body with PCM at home and abroad, so it is urgent to strengthen the research work in this field. In this paper, paraffin microcapsules were chosen as the PCM and directly blended with the backfill materials to create backfill specimens. These specimens were then subjected to experimental testing to assess their mechanical and thermal properties. The research also examined and analyzed the impact of paraffin percentage and slurry concentration on various mechanical and thermal parameters. This study offers fundamental data for optimizing the composition of the backfill slurry and for investigating the heat storage and heat release performance of the backfill body.

2. Experiment and Test

2.1. Material Preparation

In this experiment, a mixture of iron ore tailings and cement was employed as the fundamental backfill material. The particle size distribution of the tailings is as follows: $d_{30} = 70 \mu\text{m}$, $d_{50} = 90 \mu\text{m}$, $d_{99} = 250 \mu\text{m}$. The PCM selected in this study is spherical paraffin microcapsules with paraffin as the core and polymethyl methacrylate (PMMA) as the shell. The phase transition temperature is 30 °C and the particle size is 5 to 10 μm . Paraffin wax is widely used in the construction industry due to its high latent heat of phase change; almost no cooling, stable chemical properties, self-nucleation and no phase separation. The physical properties are shown in Table 1. PMMA, also known as organic glass, has a density of approximately 1.15–1.19 g/cm³; it has the characteristic of high mechanical strength, with a softening point and temperature of about 100 °C and 360 °C, respectively, both higher than the melting point of paraffin. As a result, PMMA as a microcapsule can maintain non-deformation when paraffin melts, providing encapsulation and protection for paraffin. In this experiment, paraffin microcapsules were directly added to the backfill material and thoroughly mixed with water to form a slurry. The paraffin microcapsules were directly added into backfill materials and stirred, mixed uniformly with water for preparing the slurry, taking a cement–sand mass ratio of 1:6, slurry mass concentration of 68%, 70% and 72%, and paraffin mass fraction of 0%, 5% and 10%, respectively.

Table 1. The physical properties of paraffin.

Material	Color	Physical State	Melting Point (°C)	Relative Density (g/cm ³)	Specific Heat Capacity (J/(g·K))	Heat of Melting (J/g)	Thermal Conductivity W/(m·K)
Paraffin	White	Waxy solid	47–64	0.86–0.94	2.14–2.9	200~220	0.1–0.5

(1) Sample production

Prepare the tailings, 42.5 cement, water and the shaped phase-change materials to be used, and adjust the various experimental equipment such as electronic scales, constant temperature and humidity chambers to the optimal state.

Prepare the corresponding slurry according to the designed concentration and lime sand ratio. Before loading into the trial mold, a thin layer of mineral oil or other non-reactive lubricants or engine oil should be applied to the inner surface of the trial mold to facilitate demolding. After preparing the slurry, it should be poured into the mold in a short period of time, generally not exceeding 15 min. After the slurry is filled into the mold, the heat storage filling slurry naturally settles. After its initial setting, the burrs on the surface of the mold are scraped off, and the test block is preliminarily self-supporting before the demolding treatment. When making test specimens, the age is 28 days. After each batch of molds is completed, the test blocks are numbered, cleaned and the molds are organized for the next set of experiments.

(2) Curing of specimens

After the first solidification of the sample, pour the slurry into the mold. Then, demold it and place it in the HWS-80 standard maintenance box (Beijing Zhongxingweiye Instrument Co., Ltd., Beijing, China), which has a temperature of 20 ± 2 °C and a relative humidity of over 95%. Obtain test values from samples that have been cured for 28 days. The average of the test values of three samples is the test value.

2.2. Testing Methods

To ensure that the uniaxial compressive strength of the filling body still meets the mechanical properties of filling mining, this paper uses the C43.504 MTS electronic universal testing machine (Mechanical Testing & Simulation, Eden Prairie, America) to conduct uniaxial compressive strength testing on filled test blocks. The detailed testing parameters are a testing temperature of 20 °C, testing humidity of 65%, testing stress rate of 0.500 MPa/s, testing strain rate of 0.0001 s^{-1} and testing speed of 1.000 mm/min.

Calculate the specific heat capacity of the material using a DSC tester with model Q2000 (TA Instruments, New Castle, America), and perform thermal property measurements using a differential scanning calorimeter. The scanning temperature range is -175 °C to 725 °C, with a heating rate of 1 °C/min and static nitrogen protection, with an error of $\pm 2.0\%$.

ATC 3000E thermal conductivity instrument was used to test the thermal conductivity of specimens by using the transient hot wire method; the resolution reached 0.0005 W/(m·K) and the accuracy was $\pm 3\%$.

The mass loss was measured using the Mettler Toledo TGA Star System (METTLER TOLEDO, Zurich, Switzerland) at different heating rates (1 °C/min, 5 °C/min, 10 °C/min), with a weighing accuracy of 0.005% and a weighing accuracy of 0.0025% .

The preparation, maintenance and testing of backfill specimens are shown in Figure 1.

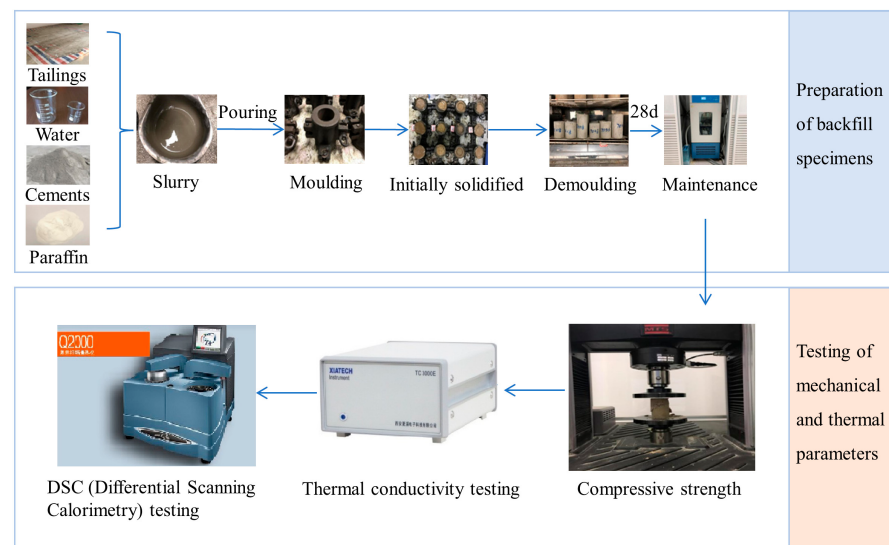


Figure 1. The preparation, maintenance and testing of backfill specimens.

3. Test and Analysis on Mechanical Properties of Backfill Specimens

3.1. Analysis on Compressive Strength of Specimens

The uniaxial compressive strengths of different backfill specimens are shown in Figure 2. It suggests that as the paraffin percentage rises, the compressive strength progressively falls. For slurry concentrations of 68%, 70% and 72%, the compressive strength drops by approximately 25.6%, 23.3% and 18.7%, in turn with when the paraffin percentage rises from 0% to 10%. It decreases from 0.508 MPa to 0.378 MPa, from 1.419 MPa to 1.089 MPa and from 2.502 MPa to 2.034 MPa, respectively. The reason is analyzed as follows: the compressive strength falls as the paraffin percentage increases because the internal framework of the backfill specimen becomes more porous and looser, intermolecular aggregation is decreased and the force required to break the intermolecular force steadily diminishes. Data analysis shows that a higher mud concentration reduces the decrease of compressive strength related to the increase of paraffin percentage.

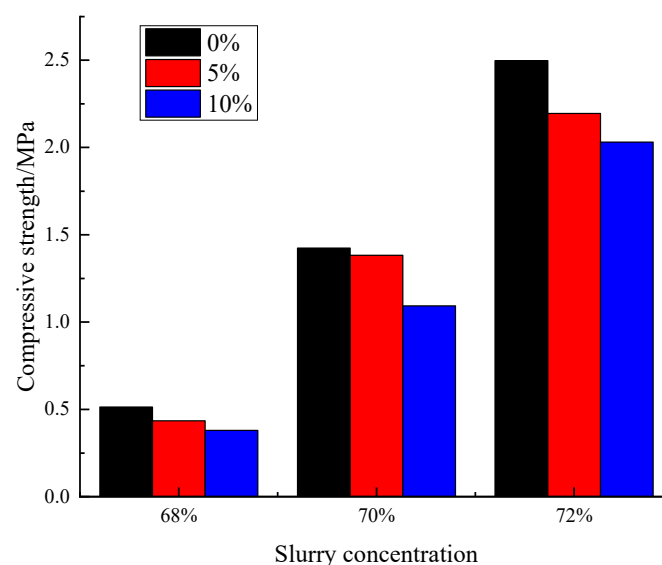


Figure 2. The uniaxial compressive strengths of backfill specimens.

Figure 2 also indicates that the compressive strength significantly increases with an increasing slurry concentration. When the paraffin wax percentage is 0%, 5% and 10%, respectively, and the slurry concentration is 68%, the compressive strength is 0.508 MPa,

0.434 MPa and 0.378 MPa, respectively. When the slurry concentration is increased to 72%, the compressive strength is 2.502 MPa, 2.198 MPa and 2.034 MPa, respectively, increasing by 3.93, 4.06- and 4.38-times year-on-year. The reason is analyzed as follows: with the increase of slurry concentration, the internal structure of the backfill specimen becomes more compact, intermolecular aggregation is enhanced and the needed force for destroying intermolecular force gradually increases, so the compressive strength increases. The data analysis shows that for the same increase in slurry concentration, the larger the paraffin percentage, the greater the increased degree of compressive strength.

Therefore, the analysis on compressive strength indicates that when PCMs are added into backfill materials, the compressive strength of the backfill specimen is weakened; however, the compressive strength is more than 1.0 MPa for all specimens with a slurry concentration of more than 70%, so the weakening effect of PCMs on compressive strength can be effectively improved by the increase of slurry concentration.

3.2. Slurry Proportion Porosity, Porosity Fractal Dimension and Mechanical Response

The porosity, porosity fractal dimension and compressive strength of backfill specimens under different paraffin percentages are shown in Figure 3. It indicates that the porosity and porosity fractal dimension increase significantly with the increase of paraffin percentage. When the paraffin percentage increases from 0% to 10%, the porosity increases about 69%, 99% and 103%, respectively, for slurry concentrations of 68%, 70% and 72%, and the porosity fractal dimension increases by about 1.15% on average. It can be seen that the internal structure of the backfill body becomes looser and more porous, the intermolecular cohesion is weakened and the compressive strength of the backfill body gradually decreases with the increase of paraffin percentage. From the response relation between porosity and mechanical property, porosity obviously decreases with the increase of slurry concentration. For a slurry concentration of 72%, when the paraffin percentage increases from 0% to 5% and from 5% to 10%, the porosity increases by 166% and 123%, respectively, and the increase ratio decreases in the second half. This does not seem to reflect that the larger the paraffin percentage, the greater the increased degree of compressive strength for the same increase of slurry concentration. This is explained as the larger the slurry concentration, the larger the proportion of solid particles and the more uniform the particle distribution, which is conducive to the crushing of large pores and the formation of small pores, and its structure is denser, which is beneficial to the improvement of the compressive strength of backfill body. In addition, when paraffin is added, it produces aggravation of the uneven distribution of solid particles inside the backfill material, which increases the size difference between large pores and small pores, deteriorates the degree of pore homogenization, and decreases the compressive strength of the backfill body.

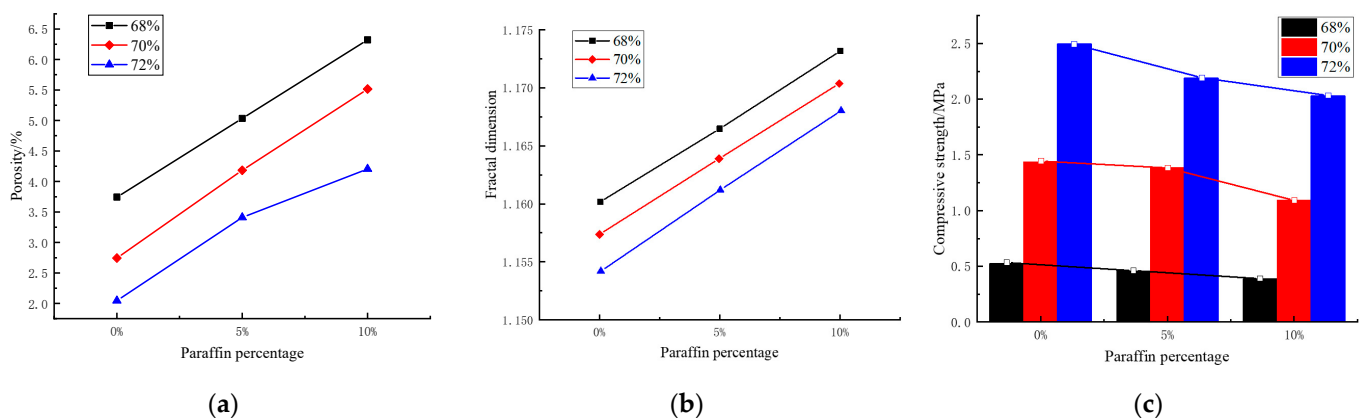


Figure 3. Porosity, fractal dimension and compressive strength for different paraffin percentages. (a) Porosity; (b) fractal dimension; (c) compressive strength.

The porosity, porosity fractal dimension and compressive strength of backfill specimens under different slurry concentrations are shown in Figure 4. It indicates that the porosity and porosity fractal dimensions decrease significantly with the increase of slurry concentration. When the slurry concentration increases from 68% to 72%, the porosity decreases about 44%, 31% and 33%, respectively, for the paraffin percentage of 0%, 5% and 10%, and the porosity fractal dimension decreases about 0.45% on average. It can be seen that the proportion of solid particles increases with the increase of slurry concentration, the spacing between particles decreases continuously and some pores are gradually enriched, reduced or even disappear caused by the interdependence and intertwining among particles. It is more conducive to the crushing of large pores and the formation of small pores, the number of small pores increases, the size difference between pores decreases and the degree of pore homogenization increases, so the structure of the backfill body is denser and the compressive strength increases.

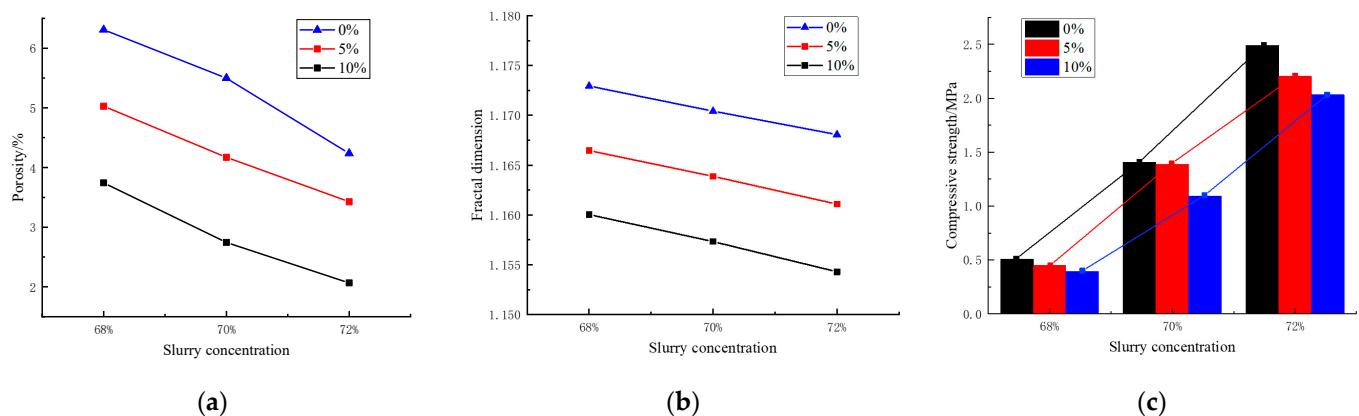


Figure 4. Porosity, fractal dimension and compressive strength for different slurry concentrations. (a) Porosity; (b) fractal dimension; (c) compressive strength.

4. Test and Analysis on Mechanical Properties of Backfill Specimens

In phase-change heat storage backfill, the heat storage capacity and heat storage rate of the backfill body are directly affected by its thermal properties. As the important thermal parameters, the density, thermal conductivity, specific heat capacity, specific enthalpy and thermogravimetry of backfill specimens should be tested and analyzed.

4.1. Thermal Conductivity

The thermal conductivities of different backfill specimens are shown in Figure 3. It indicates that the thermal conductivity decreases with an increasing paraffin percentage and the decrease is obvious, especially when the paraffin percentage increases from 0% to 5%. When the paraffin percentage increases from 0% to 10%, the thermal conductivity decreases from 0.5833 W/(m·°C) to 0.3453 W/(m·°C), from 0.6287 W/(m·°C) to 0.3651 W/(m·°C) and from 0.6716 W/(m·°C) to 0.3453 W/(m·°C), respectively. For slurry concentration of 68%, 70% and 72%, it decreases by about 40.8%, 41.9% and 48.6% successively, and the thermal conductivity decreases by an average of 34.7% for a paraffin percentage increasing from 0% to 5%. As the percentage of paraffin increases, the reduction in thermal conductivity increases with the slurry concentration. Since paraffin microcapsules were added, the internal structure of the backfill specimen becomes looser and more porous, which affects the compactness and continuity of the microstructure. In addition, the thermal conductivity of paraffin itself is low. These factors decrease the thermal conductivity of the backfill specimen with paraffin microcapsules added. It can be seen that the addition of paraffin microcapsules reduces the rate of heat storage and heat release of the backfill body.

Figure 5 also indicates that the thermal conductivity slightly increases with an increasing slurry concentration, but the influence of slurry concentration on thermal conductivity is not obvious for a paraffin percentage of 10%. When the slurry concentration increases from

68% to 72%, the thermal conductivity increases from 0.5833 W/(m·°C) to 0.6716 W/(m·°C) and from 0.3743 W/(m·°C) to 0.4428 W/(m·°C) for a paraffin percentage of 0% and 5%, and it increases by about 15.1% and 18.3% successively. The internal structure of the backfill specimen becomes more compact due to the larger slurry concentration; the compactness and continuity of the microstructure are improved, so the thermal conductivity increases. However, when the paraffin percentage is larger, the porous and loose structure caused by paraffin microcapsules is difficult to improve by the increase of slurry concentration. In addition, the mass of paraffin with low thermal conductivity also increases, so the effect of the increase of slurry concentration on thermal conductivity is not obvious. In response to the study in this article, the addition of paraffin microcapsules resulted in a decrease in the thermal conductivity of the filling material at the same slurry concentration. Zhang et al. [32] used graphite, copper powder, steel slag powder and gasification slag as substitutes for tailings when the addition amount increased to 10%. The slurry concentration was 70%, and the ash to sand ratio was 1:4. The thermal conductivity increased to 1.11 W/(m·K), 0.87 W/(m·K), 0.85 W/(m·K) and 0.83 W/(m·K), with an increase of 60.2%, 25.4%, 22.5% and 19.7%, respectively. Therefore, while meeting the compressive strength conditions, it is still necessary to search for phase-change materials with better thermal conductivity in the future.

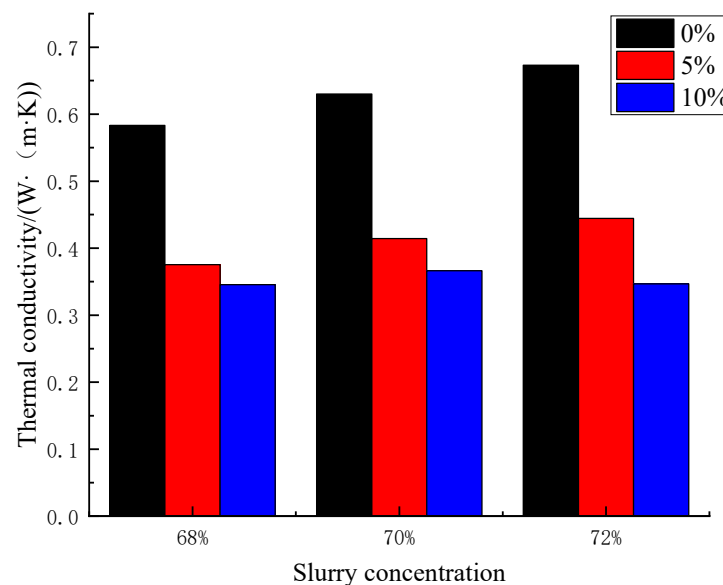


Figure 5. The thermal conductivities of backfill specimens.

4.2. Specific Heat Capacity

Figure 6 shows the variations of the specific heat capacity at a constant pressure with temperature for different backfill specimens. It indicates that the specific heat capacity gradually increases with rising temperature; the average increment is 67 J/(kg·°C) in the temperature range of 20 °C~50 °C. The figure also shows that the specific heat capacity increases with an increasing paraffin percentage at a certain temperature. At a phase-change temperature of 30 °C, when the paraffin content is 0%, 5% and 10%, and the slurry concentration is 68%, the specific heat capacity is 1.113, respectively, $\times 10^3$ J/(kg·°C), 1.126×10^3 J/(kg·°C) and 1.138×10^3 J/(kg·°C). When the slurry concentration increases to 72%, the specific heat capacities are 1.190, respectively, $\times 10^3$ J/(kg·°C), 1.234×10^3 J/(kg·°C) and 1.246×10^3 J/(kg·°C), the greater the year-on-year increase in specific heat capacity. As a phase-change material, paraffin wax has good heat storage performance and large specific heat capacity under constant pressure, so the increase of paraffin wax percentage makes the backfill sample have a large specific heat capacity.

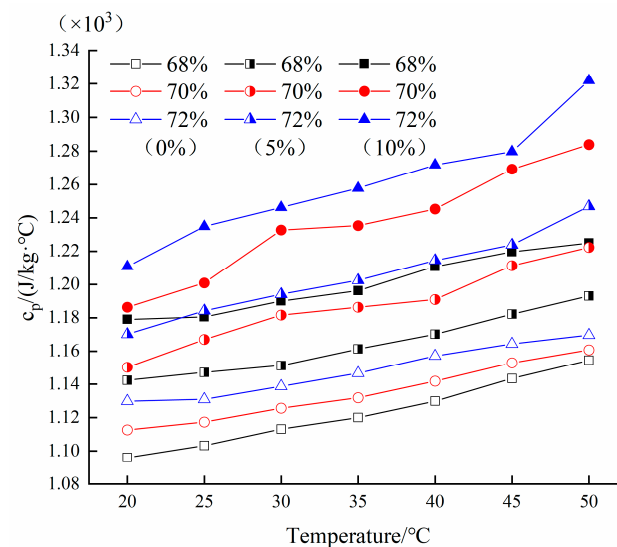


Figure 6. The variations of specific heat capacity with temperature for different backfill specimens.

Figure 6 also shows that the specific heat capacity increases with an increasing slurry concentration at a certain temperature. At a phase-change temperature of 30 °C, when the slurry concentration increases from 68% to 72%, the specific heat capacity increases from 1.113×10^3 J/(kg·°C) to 1.138×10^3 J/(kg·°C), from 1.151×10^3 J/(kg·°C) to 1.193×10^3 J/(kg·°C) and from 1.190×10^3 J/(kg·°C) to 1.246×10^3 J/(kg·°C), respectively, for paraffin percentages of 0%, 5% and 10%, and it increases by about 2.2%, 3.6% and 4.7% successively. The larger the paraffin percentage, the greater the increase degree of specific heat capacity with increasing slurry concentration. For the same paraffin percentage, the slurry concentration is larger; then, it solidifies into the backfill body with a more compact structure and larger specific heat capacity.

The effect of paraffin percentage and slurry concentration on specific heat capacity has a similar variation rule at other temperatures before and after the phase change. The sensible heat storage capacity of backfill materials can be enhanced by increasing both the slurry concentration and the paraffin percentage. Moreover, the increase in specific heat capacity that occurs with an increasing paraffin percentage is more pronounced than the increase in specific heat capacity that occurs with an increasing slurry concentration. Based on heat transfer theory, Zhang et al. [33] used FLUENT 18.0 simulation software to establish a three-dimensional unsteady heat transfer model of the heat storage/release process of the filling material and analyzed the effect of paraffin addition ratio on the heat storage of the filling material. The results showed that the average temperature of the filling body with 5% and 10% paraffin added showed an increasing trend. During the heat storage stage, the heat storage capacity of the filling body without paraffin added was 13.18×10^3 kJ, while the heat storage capacity in the filled body with 5% and 10% paraffin added is 14.40×10^3 kJ, 15.59×10^3 kJ, respectively. Compared to the filling material without added paraffin, the heat storage capacity increased by 1.22, respectively, $\times 10^3$ kJ, 2.41×10^3 kJ. The results have proven that this study is feasible and has a certain guiding significance for engineering applications.

4.3. Thermogravimetric Analysis

Figure 7 shows the variations of mass loss with temperature for different backfill specimens (temperature rise rate of 1 °C/min). The figure shows that the backfill specimens will occur mass loss whether paraffin microcapsules are added or not after a phase-change temperature of 30 °C. When the temperature rise rate is constant, the larger the paraffin percentage and the more the mass loss of specimens with the temperature rising. When the temperature rises from 30 °C to 70 °C with a temperature rise rate of 1 °C/min, for paraffin percentages of 0%, 5% and 10%, the mass loss of the specimen is about 2.8%, 4.3% and

5.8%, respectively, at a slurry concentration of 68%; about 5.0%, 5.2% and 6.0%, respectively, at a slurry concentration of 70%; and about 4.1%, 4.5% and 5.9%, respectively, at a slurry concentration of 72%. The data analysis shows that there is no obvious rule about slurry concentration influencing the mass loss of specimens. In addition, it can be seen that the higher the temperature, the more the mass loss of specimens, and also the greater the difference of mass loss for specimens with different paraffin percentages. This means that the structural stability of the backfill specimens is gradually getting worse with the increase of paraffin percentage.

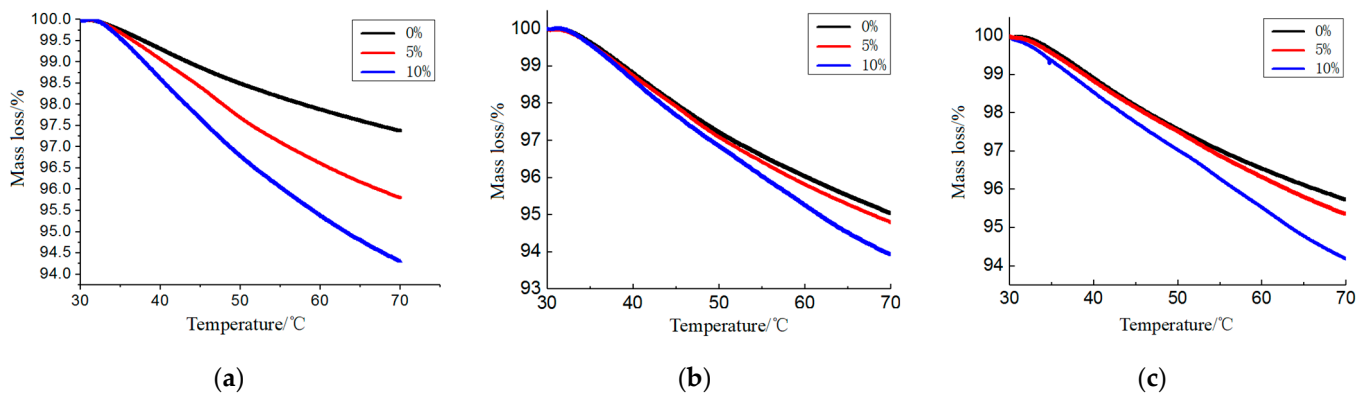


Figure 7. Mass loss for different backfill specimens (temperature rise rate of 1 °C/min). (a) Slurry concentration of 68%; (b) slurry concentration of 70%; (c) slurry concentration of 72%.

Figure 8 shows the variations of mass loss with temperature for the backfill specimens at different temperature rise rates (slurry concentration of 68%). The figure shows that the faster the temperature rise rate, the less the mass loss of specimens. For the specimen with the slurry concentration of 68% and paraffin percentage of 5%, when the temperature rises from 30 °C to 70 °C, the mass loss of the specimen is about 4.3%, 1.4% and 0.95%, respectively; at a temperature rise rate of 1 °C/min, 5 °C/min and 10 °C/min, the mass loss of other samples has a similar rule. Moreover, the figure also shows that the mass loss of specimens with paraffin added is closer to each other at the faster temperature rise rate; namely, the influence of paraffin percentage on the mass loss of specimens with paraffin added becomes smaller at the faster temperature rise rate.

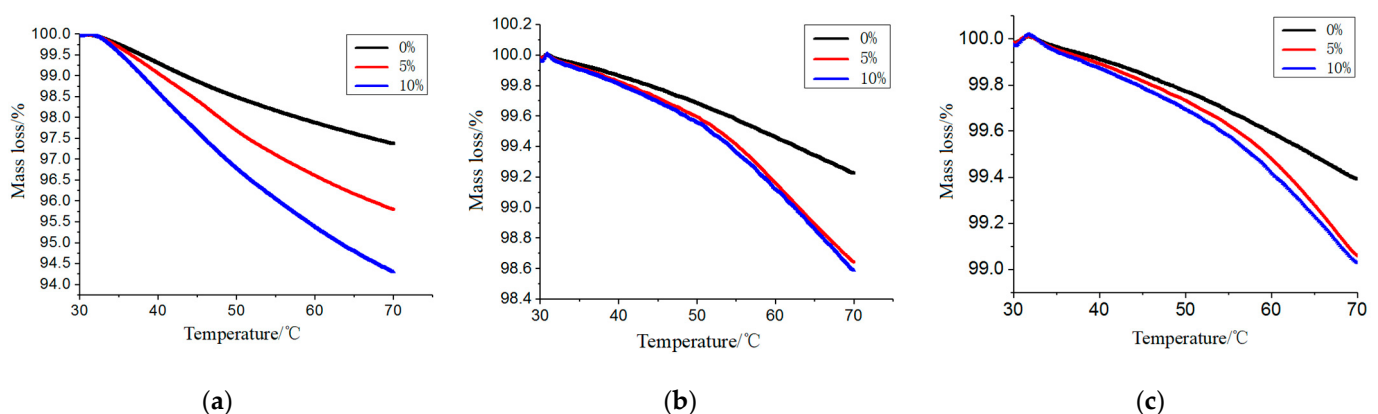


Figure 8. Mass loss for different temperature rise rates (slurry concentration of 68%). (a) Temperature rise rate of 1 °C/min; (b) temperature rise rate of 5 °C/min; (c) temperature rise rate of 10 °C/min.

5. Conclusions

The mechanical and thermal properties of backfill specimens with different paraffin percentages and different slurry concentrations were experimentally tested and analyzed. The resulting deductions were made:

(1) The compressive strength of backfill specimens gradually decreases with an increasing paraffin percentage while significantly increasing with an increasing slurry concentration. When the paraffin percentage increases from 0% to 10%, the compressive strength decreases by an average of 22.5%; when the slurry concentration increases from 68% to 72%, the compressive strength increases by an average of 4.12 times. Increasing the concentration of slurry can effectively improve the weakening effect of PCMs on compressive strength.

(2) The porosity and porosity fractal dimension increases with the increase of paraffin percentage while decreasing with the increase of slurry concentration. As the percentage of paraffin increases, it is evident that the internal structure of the backfill body becomes more porous and looser, and that its compressive strength gradually declines. As the concentration of slurry increases, so does the proportion of solid particles and the degree of pore homogenization; consequently, the backfill body's structure becomes denser and its compressive strength increases.

(3) The thermal conductivity of the backfill specimens decreases with an increasing paraffin percentage and the decrease is obvious especially when the paraffin percentage increases from 0% to 5%, it decreases by an average of 43.8% for a paraffin percentage increasing from 0% to 10% and of 34.7% for a paraffin percentage increasing from 0% to 5%. The addition of paraffin microcapsules reduces the rate of heat storage and heat release of the backfill body.

(4) The specific heat capacity of the backfill specimens gradually increases with rising temperature; the average increment is $67 \text{ J}/(\text{kg} \cdot ^\circ\text{C})$ in the temperature range of 20°C – 50°C . The specific heat capacity increases with an increasing paraffin percentage and slurry concentration. At the phase-change temperature of 30°C , when the paraffin percentage increases from 0% to 10%, the specific heat capacity increases by an average of 8.7%; when the slurry concentration increases from 68% to 72%, the specific heat capacity increases by an average of 3.5%. The increases in paraffin percentage and slurry concentration can both improve the sensible heat storage capacity of backfill materials.

In deep mining under high pressure and high temperature, adding phase-change material to tailings will make it more efficient in a heat exchange, but its thermal properties will be affected by the environment, and its mechanical properties are another key research of filling materials. Therefore, it is necessary to further test and analyze the two properties of backfilling materials at different temperatures in the later research stage to obtain their characteristics change with temperature. Moreover, the changes of sensible heat and latent heat are included in the process of heat storage and heat release of the backfill body, so it is also necessary to further investigate the variation characteristics of specific heat capacity and specific enthalpy with influencing factors, so as to provide the more complete basic data for phase-change heat storage backfill in mines.

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References

- Liu, L.; Xin, J.; Zhang, B.; Zhang, X.Y.; Wang, M.; Qiu, H.F. Basic theory and application exploration of functional filling in mines. *Chin. J. Coal Sci.* **2018**, *7*, 1811–1820.
- Cheng, A.; Shu, P.; Deng, D.; Zhou, C.; Huang, S.; Ye, Z. Microscopic acoustic emission simulation and fracture mechanism of cemented tailings backfill based on moment tensor theory. *Constr. Build. Mater.* **2021**, *308*, 125069. [\[CrossRef\]](#)
- Li, N.; Lv, S.; Wang, W.; Guo, J.; Jiang, P.; Liu, Y. Experimental investigations on the mechanical behavior of iron tailings powder with compound admixture of cement and nano-clay. *Constr. Build. Mater.* **2020**, *254*, 119259. [\[CrossRef\]](#)
- Zhou, N.; Du, E.; Zhang, J.; Zhu, C.; Zhou, H. Mechanical properties improvement of Sand-Based cemented backfill body by adding glass fibers of different lengths and ratios. *Constr. Build. Mater.* **2021**, *280*, 122408. [\[CrossRef\]](#)
- Qiu, H.; Liang, C.; Tu, B.; Liu, L.; Zhang, F.; Lv, W. Study on mechanical properties of cemented backfill with different mineral admixtures. *Constr. Build. Mater.* **2023**, *367*, 130251. [\[CrossRef\]](#)
- Wang, H.; Feng, G.; Qi, T.; Gao, X.; Wang, C.; Wang, L.; Zhang, Z. Influence of the use of corn straw fibers to connect the interfacial transition zone with the mechanical properties of cemented coal gangue backfill. *Constr. Build. Mater.* **2023**, *367*, 130334. [\[CrossRef\]](#)
- Song, X.; Hao, Y.; Wang, S.; Zhang, L.; Liu, W.; Li, J. Mechanical properties, crack evolution and damage characteristics of prefabricated fractured cemented paste backfill under uniaxial compression. *Constr. Build. Mater.* **2022**, *330*, 127251. [\[CrossRef\]](#)
- Xie, G.; Suo, Y.; Liu, L.; Yang, P.; Qu, H.; Zhang, C. Pore characteristics of sulfate-activated coal gasification slag cement paste backfill for mining. *Environ. Sci. Pollut. Res.* **2023**, *30*, 114920–114935. [\[CrossRef\]](#)
- Zhang, X.; Xu, M.; Liu, L.; Huan, C.; Zhao, Y.; Qi, C.; Song, K.I. Experimental study on thermal and mechanical properties of cemented paste backfill with phase change material. *J. Mater. Res. Technol.* **2020**, *9*, 2164–2175. [\[CrossRef\]](#)
- Zhang, X.; Cao, T.; Liu, L.; Bu, B.; Ke, Y.; Du, Q. Experimental study on thermal and mechanical properties of tailings-based cemented paste backfill with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ /expanded vermiculite shape stabilized phase change materials. *Int. J. Miner. Metall. Mater.* **2023**, *30*, 250–259. [\[CrossRef\]](#)
- Ning, P.; Ju, F.; Xiao, M.; He, Z.; Wang, D. Study on the thermal-mechanical properties and heat transfer characteristics of heat storage functional backfill body. *Geothermics* **2023**, *109*, 102654. [\[CrossRef\]](#)
- Wan, R.; Shen, L.; Liu, H.; Ma, S.; Duan, S.; Kong, D.; Zheng, C. Effect of shape-stable phase change materials on heat transfer characteristics of ground source heat pump backfill materials. *Geothermics* **2023**, *110*, 102672.
- Beiranvand, M.; Mohaghegh, M.R. Energy analysis and simulation of PCM-enhanced building envelopes in commercial buildings: A case study. *Energy Storage* **2021**, *3*, e246. [\[CrossRef\]](#)
- Islam, M.N.; Ahmed, D.H. Delaying the temperature fluctuations through PCM integrated building walls—Room conditions, PCM placement, and temperature of the heat sources. *Energy Storage* **2021**, *3*, e245. [\[CrossRef\]](#)
- Kabdrakhmanova, M.; Memon, S.A.; Saurbayeva, A. Implementation of the panel data regression analysis in PCM integrated buildings located in a humid subtropical climate. *Energy* **2021**, *237*, 121651. [\[CrossRef\]](#)
- Yang, Y.; Wu, W.; Fu, S.; Zhang, H. Study of a novel ceramsite-based shape-stabilized composite phase change material (PCM) for energy conservation in buildings. *Constr. Build. Mater.* **2020**, *246*, 118479. [\[CrossRef\]](#)
- Wu, D.; Rahim, M.; El Ganaoui, M.; Djedjig, R.; Bennacer, R.; Liu, B. Experimental investigation on the hygrothermal behavior of a new multilayer building envelope integrating PCM with bio-based material. *Build. Environ.* **2021**, *201*, 107995. [\[CrossRef\]](#)
- Liu, Z.; Zang, C.; Zhang, Y.; Jiang, J.; Yuan, Z.; Liu, G.; Li, H. Mechanical properties and antifreeze performance of cement-based composites with liquid paraffin/diatomite capsule low-temperature phase change. *Constr. Build. Mater.* **2022**, *341*, 127773. [\[CrossRef\]](#)
- Alsaadawi, M.M.; Amin, M.; Tahwia, A.M. Thermal, mechanical and microstructural properties of sustainable concrete incorporating Phase change materials. *Constr. Build. Mater.* **2022**, *356*, 129300. [\[CrossRef\]](#)
- Ryms, M.; Januszewicz, K.; Hausteine, E.; Kazimierski, P.; Lewandowski, W.M. Thermal properties of a cement composite containing phase change materials (PCMs) with post-pyrolytic char obtained from spent tyres as a carrier. *Energy* **2022**, *239*, 121936. [\[CrossRef\]](#)
- Yu, K.; Liu, Y.; Yang, Y. Review on form-stable inorganic hydrated salt phase change materials: Preparation, characterization and effect on the thermophysical properties. *Appl. Energy* **2021**, *292*, 116845. [\[CrossRef\]](#)
- Lian, P.; Yan, R.; Wu, Z.; Wang, Z.; Chen, Y.; Zhang, L.; Sheng, X. Thermal performance of novel form-stable disodium hydrogen phosphate dodecahydrate-based composite phase change materials for building thermal energy storage. *Adv. Compos. Hybrid Mater.* **2023**, *6*, 74. [\[CrossRef\]](#)
- Ong, P.J.; Leow, Y.; Soo, X.Y.D.; Chua, M.H.; Ni, X.; Suwardi, A.; Zhu, Q. Valorization of Spent coffee Grounds: A sustainable resource for Bio-based phase change materials for thermal energy storage. *Waste Manag.* **2023**, *157*, 339–347. [\[CrossRef\]](#) [\[PubMed\]](#)
- Gencel, O.; Sari, A.; Kaplan, G.; Ustaoglu, A.; Hekimoğlu, G.; Bayraktar, O.Y.; Ozbakkaloglu, T. Properties of eco-friendly foam concrete containing PCM impregnated rice husk ash for thermal management of buildings. *J. Build. Eng.* **2022**, *58*, 104961. [\[CrossRef\]](#)
- Sobolciak, P.; Karkri, M.; Al-Maadeed, M.A.; Krupa, I. Thermal characterization of phase change materials based on linear low-density polyethylene, paraffin wax and expanded graphite. *Renew. Energy* **2016**, *88*, 372–382. [\[CrossRef\]](#)
- Xiang, B.; Yang, Z.; Zhang, J. ASA/SEBS/paraffin composites as phase change material for potential cooling and heating applications in building. *Polym. Adv. Technol.* **2021**, *32*, 420–427. [\[CrossRef\]](#)

27. Xie, Y.; Yang, Y.; Liu, Y.; Wang, S.; Guo, X.; Wang, H.; Cao, D. Paraffin/polyethylene/graphite composite phase change materials with enhanced thermal conductivity and leakage-proof. *Adv. Compos. Hybrid Mater.* **2021**, *4*, 543–551. [[CrossRef](#)]
28. Chen, F.; Wolcott, M. Polyethylene/paraffin binary composites for phase change material energy storage in building: A morphology, thermal properties, and paraffin leakage study. *Sol. Energy Mater. Sol. Cells* **2015**, *137*, 79–85. [[CrossRef](#)]
29. Wang, F.; Zheng, W.; Qiao, Z.; Qi, Y.; Chen, Z.; Li, H. Study of the structural-functional lightweight concrete containing novel hollow ceramsite compounded with paraffin. *Constr. Build. Mater.* **2022**, *342*, 127954. [[CrossRef](#)]
30. Wang, Y.; Li, Q.; Miao, W.; Su, Y.; He, X.; Strnadel, B. The thermal performances of cement-based materials with different types of microencapsulated phase change materials. *Constr. Build. Mater.* **2022**, *345*, 128388. [[CrossRef](#)]
31. Gbekou, F.K.; Benzarti, K.; Boudenne, A.; Eddhahak, A.; Duc, M. Mechanical and thermophysical properties of cement mortars including bio-based microencapsulated phase change materials. *Constr. Build. Mater.* **2022**, *352*, 129056. [[CrossRef](#)]
32. Zhang, X.; Wen, D.; Zhao, Y.; Liu, L.; Zhang, B.; Huan, C.; Wang, M.; Tu, B. Thermal mechanical performance and heat transfer process of mine thermal storage/energy storage filling materials. *J. Coal Sci.* **2021**, *46*, 3158–3171.
33. Zhang, X.; Liu, L. Preparation and Thermology-Mechanics Properties of Filling Material Based on Mine Tailing with Heat Storage Function. Master's Thesis, Xi'an University of Science and Technology, Xi'an, China, July 2020.

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