

Waste Cellular Concrete for Preparation of Shape-Stable Phase Change Materials

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ABSTRACT

In order to absorb urban solid waste on a large scale and reduce the damage to the urban ecological environment caused by the massive accumulation of waste cellular concrete (WCC). In this work, WCC was used as skeleton material, which was pretreated, and sodium carbonate was used as phase change material to prepare shape-stable phase change materials (SSPCMs). The results show that the calcinated WCC could load with 45 wt.% Na_2CO_3 . The melting latent heat of the SSPCM loading with 40 wt.% Na_2CO_3 was 20.45 J/g measured by differential scanning calorimeter (DSC) and the maximum thermal conductivity of the SSPCM measured by Laser Flash Analysis (LFA) was 0.24 W/(m·K). X-Ray diffraction (XRD) and Fourier transform infrared (FT-IR) showed that there was good chemical compatibility between skeleton material and phase change material.

Keywords: Solid waste, shape-stable phase change material, cellular concrete, skeleton material, performance

1. INTRODUCTION

China aims to achieve carbon peak by 2030 and carbon neutral by 2060[1], the adjustment and optimization of energy structure has become one of the primary tasks of energy. Compared with developed countries, the energy utilization of China is low, and energy waste has become one of the biggest problems in the energy field. Developing renewable energy and improving energy efficiency is an effective way to solve the energy crisis and environmental pollution. The field of thermal energy is an important branch in the field of energy.

There are three main types of Thermal Energy Storage techniques, namely the sensible heat storage,

the latent heat storage and the thermochemical heat storage. As we know, the sensible heat storage technique is mature but its thermal energy storage density is very low while the thermochemical heat storage technique is still in laboratory stage. The latent heat storage technique has not only the high thermal storage density, the constant charging and discharging temperature variation but the small space requirement. However, supercool, phase separation and low thermal conductivity of the phase change materials (PCMs) limits their large-scale applications of the latent heat storage technique in real engineering. To overcome the demerits of the latent heat storage and the sensible heat storage, the novel shape-stable phase change materials (SSPCMs) based on both the latent heat storage and sensible heat storage have been proposed[2]. Inside the SSPCMs the skeleton materials microencapsulate the PCMs in microporous and mesoporous to decrease the supercool and phase separation, increase the thermal conductivity and avoid the PCM leakage. Li et al. [3] compared the shape-stable PCM composites with alumina as skeleton material while aluminum and NaLiCO_3 as PCM, respectively and concluded that the aluminum-based composite presents a higher thermal performance than the salt composite. Solid waste is free. Rational use of them will effectively improve our living environment. Consequently, wang et al. [4] proposed the coal fly ash as the skeleton material as well as the K_2CO_3 as PCM and fabricated shape-stable PCM composites and obtained the optimal mass ratio of the coal fly ash to the K_2CO_3 . Wang et al. [5] utilized the steel slag as skeleton material as well as the solar salt (40 wt.% KNO_3 - 60 wt.% NaNO_3) as PCM and fabricated shape-stable PCM composites. They investigated the effect of PCM mass fraction on the thermal performance of shape-stable PCM composites

and concluded that the best mass ration of the steel slag to the solar salt is 5:5. Anagnostopoulos et al. [6] proposed to use red mud, an industrial waste, as the skeleton material and nitrate as PCM to prepare SSPCM. It was observed that the overall performance was good, which provided a pathway and valorization of the RM as a by-product for energy-related applications. Li et al. [7] used Expanded Perlite as skeleton material and Sodium Nitrate as PCM to fabricate shape-stable PCM composites. Sang et al. [8] proposed using ternary carbonate (K_2CO_3 - Li_2CO_3 - Na_2CO_3) as high-temperature thermal energy storage material and MgO as skeleton material to prepare the SSPCMs. The results showed that there was no chemical reaction between carbonate and MgO, and the SSPCM showed excellent thermal cycle stability after 100 cycles.

SSPCM is usually made in brick shape. In practical engineering applications, SSPCM bricks are stacked layer by layer to a height of about two meters, which can be used in light buildings to maintain building temperature. Because of its huge heat storage capacity and relatively stable phase change temperature, the building temperature can be gentle.

Cellular concrete is a new type of green building material[9], which has the characteristics of thermal insulation and good fire resistance. Therefore, waste cellular concrete (WCC), as the solid waste left during the construction or demolition of buildings, has the potential to be used as skeleton materials. Moreover, it is widely available, easy to obtain and low cost. It can be used to produce SSPCMs on a large scale. Cellular concrete is mainly composed of coal fly ash and cement. Coal fly ash as the skeleton material of SSPCMs has been studied by others, but waste concrete as the skeleton material has not been reported. Accordingly, this work studied the shape-stable phase change materials prepared by calcinated WCC as skeleton material and sodium carbonate as PCM, which laid a certain foundation for the research on the preparation of high-temperature SSPCMs by waste concrete.

2. MATERIALS AND METHODS

2.1 Raw Materials

In this work, Na_2CO_3 was used as phase change material, which was purchased from Sinopharm Chemical Reagent Co., Ltd. with purity $\geq 99\%$. The skeleton material was calcinated WCC. Polyvinyl alcohol (PVA, purity $\geq 99\%$) solution with mass fraction of 5% was used as sintering agent, which was helpful to the forming of SSPCMs.

2.2 Fabrication of SSPCMs

Firstly, the WCC was calcinated to remove impurities and organic matter. The WCC was broken up and ground into a powder, weighed and recorded. Then fired it in a muffle furnace (SX2-5-12A, China) at 900 °C for 2 h. After the muffle cooled naturally to room temperature, the calcinated WCC was removed and weighed again. Finally, the two sets of data were analyzed and the results showed that 50 g of WCC was calcinated at 900 °C for 2 h with 44.66 g remaining and the heat loss ratio was 10.68%. **Fig. 1** shows the XRD patterns of WCC before and after calcinating.

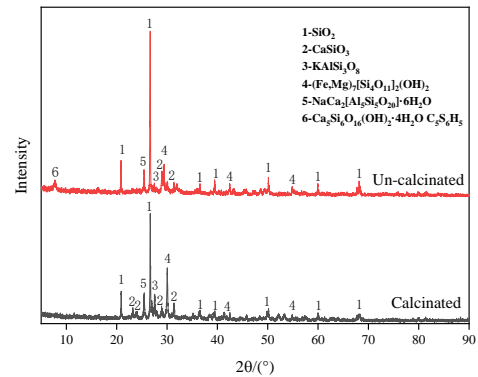


Fig. 1. The XRD patterns of WCC before and after calcinating

As can be seen from **Fig. 1**, the composition of calcinated WCC is different from that of un-calcinated WCC. The intensity of the SiO_2 diffraction peaks in un-calcinated WCC is higher than that in calcinated WCC, indicating a higher SiO_2 content in the former. In the production of cellular concrete, some fibers and organic glues are often added to the cellular concrete in order to overcome its shortcomings such as brittleness, easy of cracking and low tensile strength. These substances generally decompose at high temperatures. The decomposition of organic matter and the formation of new substances occur when the WCC was calcinating. By comparing the XRD curves before and after calcinating, it can be seen that some chemical reactions have taken place after calcinating WCC. Tobermorite was decomposed into SiO_2 and wollastonite ($Ca_3Si_3O_9$) at high temperature. Due to the low content of wollastonite, there is no diffraction peak of it. However, the small change in intensity of the diffraction peaks and the lack of change in the composition of the main physical phases suggest that the mass lost after calcinating WCC at 900°C is due to the decomposition of organic matter.

In this work, SSPCMs were fabricated by the cold-compression-hot-sintering (CCHS) method, and the fabrication process is described in **Fig. 2** as follows: Mixing the powdered Na_2CO_3 with an appropriate

amount of calcinated WCC powder in a planetary mill (KE-2L, China) at 250 r/min for 30 min to obtain the mixture powder; The mixture powdered was then poured into an agate crucible and an appropriate amount of PVA solution was added, grind until well combined; Next, weighed an appropriate amount of mixture powder and poured it into the cylindrical module with an inner diameter of 13 mm; Pressing 6 MPa for 3 min on a press machine (MSY-50, China) to obtain dense samples; Finally, the dense samples were transferred to a muffle furnace and sintered according to the following procedure: 1) Heat up from room temperature to 100 °C at a rate of 2 °C/min and holding at 100 °C for 0.5 h, which is called the drying process; 2) Heat up from 100 °C to 400 °C at a rate of 2 °C/min and holding at 400 °C for 1 h to remove PVA; 3) Heat up from 400 °C to 900 °C at a rate of 2 °C/min and holding at 900 °C holding for 1.5 h; 4) Turn off the muffle furnace and take out the final Na_2CO_3 /calcinated WCC SSPCMs (named sample NC) after the sample is naturally cooled to room temperature.

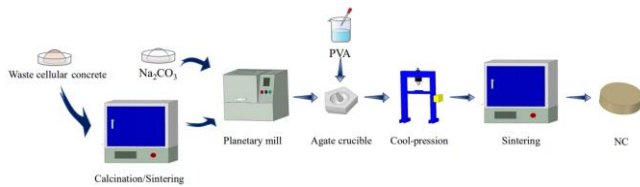


Fig. 2. Schematic diagram of the SSPCMs fabrication

Table 1 shows specific information on the five different mass ratios of the SSPCMs and Fig. 3 shows the appearance of the SSPCMs

TABLE 1 DETAILS OF DIFFERENT SSPCMS

SSPCMs	NC1	NC2	NC3	NC4	NC5
Na_2CO_3 , wt. %	60	55	50	45	40
calcinated WCC, wt. %	40	45	50	55	60
Sintering agent, wt. %	5	5	5	5	5

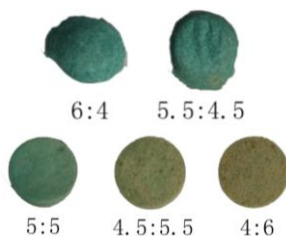


Fig. 3. Photographs of different SSPCMs after sintering

As shown in **Fig. 3**, the five SSPCMs are sample NC1, NC2, NC3, NC4 and NC5 in that order. Sample NC1 and NC2 can be clearly observed that they have severe deformation and salt leakage with a dark green color; Sample NC3 has slight deformation and a small amount of salt leakage with a green color; Sample NC4 and NC5 have the best morphological appearance because of no shape deformation and salt leakage with an earthy brown color. From the results, the samples with a mass fraction of Na_2CO_3 between 40% and 45% can be prepared perfect SSPCMs.

2.3 Characterization methods

In this work, the Synchronous Thermal Analyzer (STA 449F3, Netzsch, Germany) with differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) are used to measure the melting and solidification process, latent heat and specific heat of the SSPCCs, while Pt crucibles are used with a high-purity nitrogen (99.999%) as protection gas and purge gas. For each sample, five melting-solidification cycles are performed at an interval of 10 K/min under the nitrogen atmosphere. Thermal conductivity of the SSPCCs is calculated via the thermal diffusivity analyzed by the Laser Flash Analysis (LFA457, Netzsch, Germany) under a high-purity nitrogen (99.999%) as the protection gas and purge gas. An X-Ray diffraction (XRD, SmartLab, Rigaku, Japan) is used to check the chemical compatibility of the SSPCCs by utilizing $\text{CuK}\alpha_1$ radiation with a scanning angle over 5 and 90 ° with an interval of 0.02 °.

3. RESULTS AND DISCUSSION

3.1 Thermal energy storage analysis of SSPCMs

Fig. 4 shows the DSC curves of Na_2CO_3 , Sample NC4 and NC5, from which it can be clearly observed that both SSPCMs have a smaller latent heat of melting than Na_2CO_3 . The results of DSC showed that the melting latent heat of sample NC4 was 14.05 J/g, that of sample NC5 was 20.45 J/g, and that of Na_2CO_3 was 307.90 J/g.

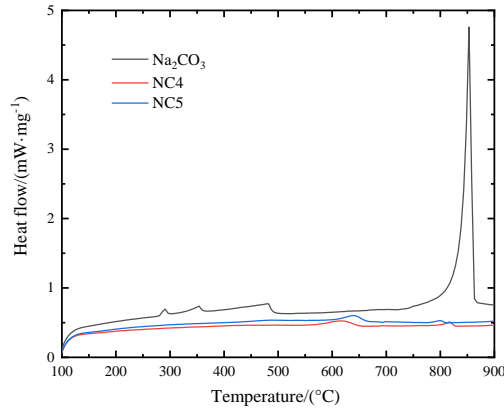


Fig. 4. DSC curves of Na_2CO_3 , NC4 and NC5

Fig. 5 shows the specific heats of Na_2CO_3 , sample NC4 and NC5 at different temperatures. The specific heat of SSPCM with higher Na_2CO_3 content is lower than that of SSPCM with lower Na_2CO_3 content, which indicates that chemical reactions may occur during the preparation of SSPCM samples in this work.

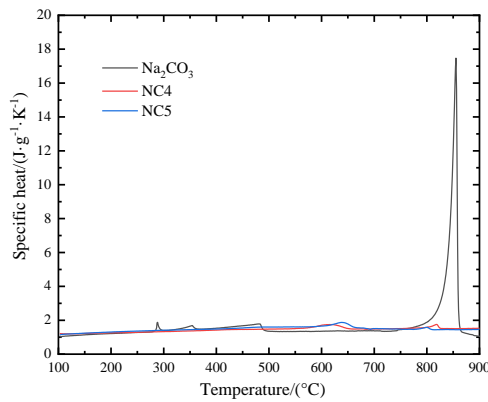


Fig. 5. Specific heat curves of Na_2CO_3 , NC4 and NC5

3.2 Thermal conductivity analysis of SSPCMs

The thermal conductivity of SSPCMs is an important parameter to evaluate heat transfer performance. In this work, the LFA was used to measure the thermal diffusivity of SSPCM, and the density of sample NC5 was accurately measured and assumed to be constant over the temperature range. The thermal conductivity of the sample NC5 was calculated by the following formula:

$$\lambda = \alpha(T)\rho(T)c_p(T)$$

Where λ is the thermal conductivity of SSPCMs, $\text{W}/(\text{m}\cdot\text{K})$; α is the thermal diffusivity of SSPCMs, m^2/s ; ρ is the density of SSPCM samples, kg/m^3 ; c_p is the specific heat of SSPCMs, $\text{J}/(\text{kg}\cdot\text{K})$.

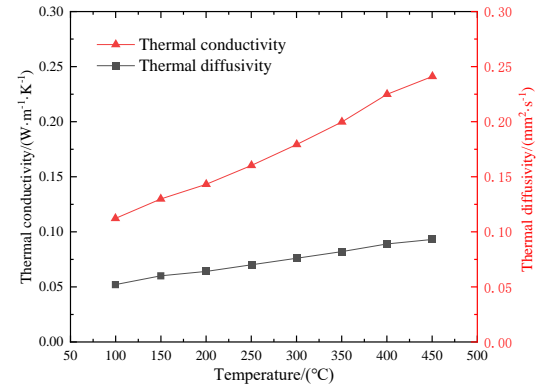


Fig. 6. Thermal conductivity and thermal diffusivity of NC5

The curves of thermal diffusivity and thermal conductivity of sample NC5 with temperature were shown in Fig. 6. It was obvious that the thermal diffusivity of the sample NC5 increased gently with temperature. Because the specific heat of the sample NC5 was increased greatly with the temperature increasing, the thermal conductivity was increased linearly with the temperature changing. Calculations showed that the thermal conductivity was $0.11 \text{ W}/(\text{m}\cdot\text{K})$ at 100°C and reached a maximum value of $0.24 \text{ W}/(\text{m}\cdot\text{K})$ at 450°C .

3.3 Chemical compatibility of SSPCMs

Fig. 7 shows the XRD patterns of Na_2CO_3 , calcinated WCC and sample NC5. The XRD pattern of sample NC5 showed that the main phase was Na_2CO_3 and the diffraction peak intensity was the highest. Mainly difference is the diffraction peak intensity of Na_2CO_3 compared with the pure Na_2CO_3 phase. The main phase composition of sample NC5 was identical to the phase composition of the calcinated WCC, which indicates that no new substances were formed between Na_2CO_3 and the calcinated WCC components during the preparation by CCHS method. Good chemical compatibility was achieved.

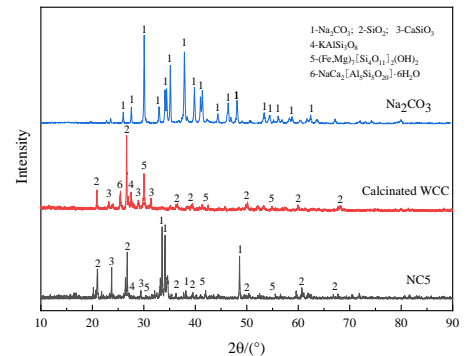


Fig. 7. The XRD patterns of Na_2CO_3 , calcinated WCC and NC5

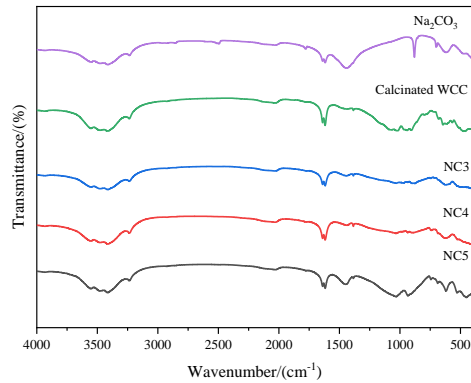


Fig. 8. The FT-IR spectra of Na_2CO_3 , calcinated WCC and SSPCMs

TABLE 2 THE CHARACTERISTIC PEAKS OF Na_2CO_3 , CALCINATED WCC AND SSPCMs

Materials	Characteristic peaks (cm^{-1})
Na_2CO_3	3413, 3235, 2030, 1777, 1617, 1446, 880
calcinated WCC	3551, 3414, 3237, 2031, 1638, 1618, 1384, 1023, 939, 904
NC3	3551, 3414, 3236, 2032, 1637, 1617, 1438, 1384, 1031, 877
NC4	3554, 3413, 3235, 2031, 1638, 1617, 1438, 1384, 1031, 934, 896
NC5	3552, 3413, 3235, 2031, 1638, 1617, 1449, 1385, 1031, 934

To verify whether the reaction between the skeleton material and PCM can occur spontaneously in the process of preparing SSPCMs, it is further analyzed and explained from the perspective of chemical bond. **Fig. 8** shows the FT-IR spectra of Na_2CO_3 , calcinated WCC and SSPCMs. Notably, it was evident from the FT-TR spectra that all Na_2CO_3 , calcinated WCC and SSPCMs exhibited crystalline water bonding (3100 cm^{-1} to 3600 cm^{-1}) in the functional group region, which might due to the absorption of water from the air during the preparation of Na_2CO_3 in SSPCMs. Other characteristic peaks of Na_2CO_3 were C=O bonding (2030 cm^{-1}), N=O bonding (1777 cm^{-1} and 1617 cm^{-1}), C-O bonding (1446 cm^{-1}) and N-O bonding (880 cm^{-1}). The main characteristic peaks of calcinated WCC were C=O bonding (2031 cm^{-1}), N=O bonding (1638 cm^{-1} and 1618 cm^{-1}), C-O bonding (1384 cm^{-1}), Si-O bonding (1023 cm^{-1}) and N-O bonding (939 cm^{-1} and 904 cm^{-1}). It could be concluded from **Fig. 8** and **Table 2** that the main characteristic peaks of sample NC3, NC4 and NC5 were essentially the same and correspond to the chemical bonds. The characteristic peaks for these samples were expressed as C=O bonding ($2031\text{ cm}^{-1}/2032\text{ cm}^{-1}$), N=O bonding (1638 cm^{-1} to 1617 cm^{-1}), C-O stretching vibration ($1438\text{ cm}^{-1}/1439\text{ cm}^{-1}$), Si-O

stretching vibration (1031 cm^{-1}) and N-O bonding (1000 cm^{-1} to 870 cm^{-1}). By comparing the characteristic peaks of the samples, Na_2CO_3 and calcinated WCC, there was no new chemical bonds created in SSPCMs. In summary, it is concluded that the samples are only bonded physically during the preparation process, that is, the chemical reaction is not reacted between the skeletal material and the PCM. They have good chemical compatibility.

4. CONCLUSIONS

In this work, calcinated WCC was used as the skeleton material and sodium carbonate was used as the PCM. The SSPCMs were fabricated by CCHS method. The main findings were as follows:

The SSPCM showed no deformation and salt leakage when loading with 45 wt.% Na_2CO_3 ; Good chemical compatibility between the calcinated WCC components and Na_2CO_3 was confirmed; The melting latent heat of SSPCM was 20.45 J/g when loading with 40 wt.% Na_2CO_3 , and the maximum thermal conductivity was $0.24\text{ W/(m}\cdot\text{K)}$.

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