# STRUCTURE REINFORCE OF CaO-BASED BODIES FOR THERMOCHEMICAL ENERGY STORAGE

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**ABSTRACT**

Thermochemical energy storage (TCES) is a novel heat storage technology with high heat storage density and capability of large-scale energy storage for a long time. This work describes a composite material which has improved mechanical and reaction properties based on $Ca(OH)_2$/CaO heat storage system. Heavy tar was used as a binder of CaO particles. The mechanical and heat transfer properties of the composite are enhanced due to the matrix carbon structure produced by tar calcination. The most suitable material (tar content of 15 wt%, calcinated in $N_2$ at 850 °C) was tested for 30 dehydration/ hydration cycles. The cyclic test shows that the composite has good mechanical and reaction properties with a crushing strength value of > 11 N and molar hydration conversion of > 90 % after 30 cycles.

**Keywords:**  Thermochemical Energy Storage, Calcium oxide, Composite material, Heavy tar

**NONMENCLATURE**

| Abbreviations | |
|---|---|
| TES | Thermal energy storage |
| TCES | Thermochemical energy storage |
| Ave | Average |

## 1. INTRODUCTION

With the development of society, the shortage of fossil energy has become an increasingly serious problem which requires the development of renewable energy and energy-saving technologies, such as solar thermal utilization and industrial waste heat recovery. However, the discontinuity and uneven distribution of solar energy and industrial waste heat have hindered their application. Thermal energy storage (TES) technology is an important means to achieve solar heat utilization, industrial waste heat recovery and carbon reduction [1-3]. Compared with sensible heat and latent heat storage, thermochemical energy storage (TCES) is a novel heat storage technology which is receiving more and more attention. Due to its larger heat storage density, ability of long-term heat storage and long-distance transportation of mass heat, TCES has a broad application prospect [4].

The $Ca(OH)_2$/CaO system in this paper is a thermochemical energy storage system which is inexpensive and readily available, thus it is particularly suitable for high temperature heat storage [5, 6].

For $Ca(OH)_2$/CaO system, there are mainly three types of reactors, namely the indirect-type, the direct-type and the continuous reactors. Many researchers have done fruitful research on the indirect-type and direct-type reactors [7]. Compared with the previous two types of reactors, the continuous reactor enables uninterrupted release of energy by importing reactant and exhausting product continually, which is more suitable for large-scale energy storage. Criado et al. [8-10] designed a reaction system based on circulating fluidized bed, which has been successfully operated under hydration and dehydration at virous conditions. Pardo et al. [11] established a standard bubbling fluid reactor using 70 wt% $Al_2O_3$ as fluidized particles. 50 cycles have been operated, which proves the feasibility of storing thermal energy with the $Ca(OH)_2$/CaO system in a fluidized bed. However, research on fluidized bed based TCES system is still in its infancy because of the crush and the uneven distribution of particle size. A good way to solve this

problem is to enhance the mechanical properties of the reactants. Criado et al. [12, 13] used sodium silicate as a binder of active CaO particles, the composites exhibited superior crushing resistance due to the formation of hard Ca silicates, which resulted from the reaction of the binder and the exterior of the CaO particles. Sakellariou et al. [14] used kaolinite as a binder in natural limestone powder to improve the mechanical properties of active particles, it is found that the structural integrity was retained due to the formation of a ternary mixed Ca/Al/Si crystal phase.

However, in order to ensure the mechanical strength of the composite material, it is often required to add a considerable amount of binder, which corresspondingly reduces the heat storage density. The main objective of this paper was to investigate ways to guarantee the mechanical properties of Ca(OH)$_2$/CaO heat storage materials with less binder usage. This requires a more effective binder with higher adhesion to generate a better supporting structure in the composite material. The heavy tar (Hereinafter referred to as tar) is a cementitious binder which can form a matrix carbon structure under high temperature pyrolysis with the catalyst addition. In this research, we firstly screened the preparation conditions and characterized the chemical composition of the composite material, including elemental analysis. Then, the performance of the composite over 30 hydration/dehydration cycles was studied to verify the cyclic stability of the material.

## 2. EXPERIMENTAL SETUP

### 2.1 Material preparation

In order to study the optimal tar addition ratio, three different addition ratios of tar-CaO mixed heat storage materials were prepared, the mass ratio of tar was 5%, 10% and 15%, respectively. The KCl was used as the catalyst. In order to ensure the matrix carbon formatiou of tar, the mass ration of KCl was set at 5%. (KCl and CaO are from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China). The details and procedures of tar-CaO composite materials preparation were shown as follows. The total sample mass was strictly controlled at 4 g in each synthesis process. Firstly, the tar, CaO and KCl were put in a 50 ml beaker. The dichloromethane was used as a solvent to ensure thorough mixing of tar and CaO. The mixture was stirred at a constant temperature of 30 °C for 1.5 h using a thermostatic stirrer manufactured by Shanghai Yangyingpu Instrument & Meter Manufacturing Co., Ltd. After the completion of the mixing, the mixture was dried at 60 °C for 2 h using a

vacuum drying oven (Shanghai Yiheng Scientific Instrument Co., Ltd.) to obtain the tar-CaO composite material. Then, the composite material was transferred to a steel compressor (radius*depth: 10 mm*30 mm). The composite was compressed at 0.1 Mpa for 10s. After the compression, the pre-prepared tar-CaO composite material was calcined in a tube furnace (Shanghai Minyue Electric Furnace Technology Co., Ltd.) at 850 ° C. High-purity nitrogen (99.999%) was used as the shielding gas with the gas flow rate of 200 ml/min in the experiment. The prepared tar-CaO composite was named as CT-N, where N is the mass fraction of tar.

### 2.2 Material characterization

The mechanical properties of the composite formulations with different tar addition ratio were measured via crushing strength (CS) measurements on a Q800 dynamic thermomechanical analyzer with the ability to measure values in the range of 0–18 N and a resolution of 0.0001 N. The mechanical properties of CT-15 with different cycles were tested in the same method.

The morphologies of CT-15 with different cycles were characterized by using scanning electron microscope (SEM, Nova NanoSEM 230 instrument, USA, FEI). In order to determine the carbon content of the composite formulations and the changes in carbon content with different cycle times, EDS analysis was carried, and the thermal conductivity was tested by using Laserflash Thermal Conductivity (LFA 467 HyperFlash, Germany, NETZSCH).

The cycling system based on tube furnace was designed to test the exothermic reaction conversion rate of CT-15 with different cycles. High-purity nitrogen (99.999%) was used as the shielding gas with the gas flow rate of 200 ml/min in the experiment.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of tar content

The crushing strength (CS) measurements of CaO with different tar addition ratio are shown in Fig. 1. According to Fig. 1, the crushing strength of the composite material is greatly improved compared with the pure CaO [14] (nearly 0.2 N). What's more, the crushing strength of the composite material increases with the increment of tar content, and the maximum crushing strength corresponds to a tar content of 15 wt%. Considering that the crushing strength and heat storage density of the material, 15 wt% is the optimal tar addition content. At this ratio, the crushing strength of the composite formulation can be effectively improved,

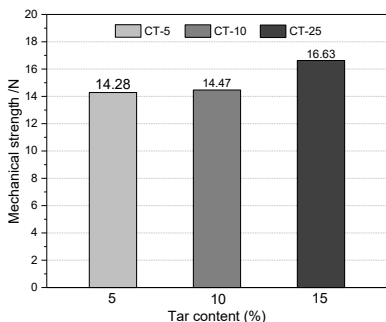(approximately 17 N), and the reduction of the heat storage density can also be acceptable.


Fig. 1 Crushing strength of composite formulatins

### 3.2 Verification of the composition and thermal conductivity of CT-15

In order to evaluate the carbon content and the morphologies of CT-15, SEM and EDS analysis were performed respectively.

Fig. 2 shows the SEM images and EDS analysis of CT-15. It can be seen from the SEM image that the surface of CaO is covered with a film-like network structure (the red cycle area in Fig. 2 (b)). According to the SEM images, this structure is considered to be a matrix carbon structure, and it is this matrix structure that enhances the mechanical properties of the composite. According to EDS analysis (Fig. 2 (c)), the mass fraction of carbon is 10.11 %, less than 15 % of tar. The reason for the mass reduction is the decomposition of organic matter during high temperature pyrolysis. Therefore, the mass fraction of CaO in the composite material is 85 %, which makes the reduction of heat storage density can be mitigated.
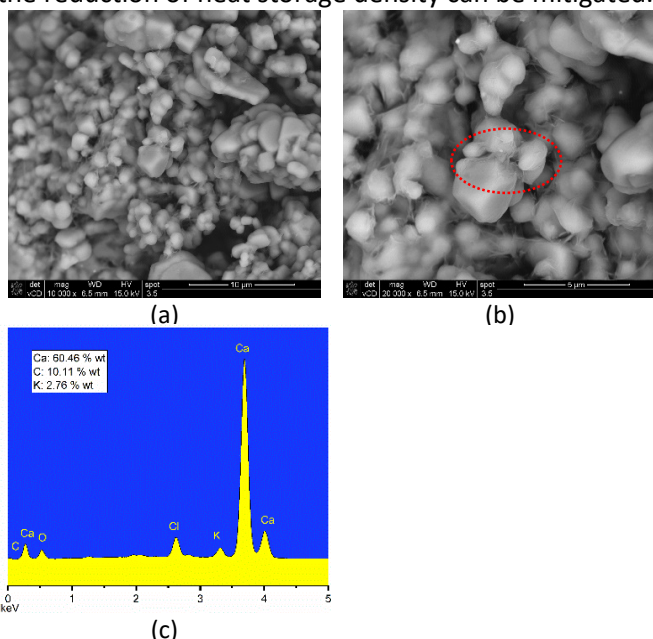

(a)                    (b)


(c)
Fig. 2 SEM images of composite formulation: (a, b) CT-15 (×10000 and×20000, respectively), and (c) EDS analysis

In order to study the effect of matrix carbon structure on the thermal storage properties of the composite, the thermal conductivity of pure CaO and CT-15 was tested (at 25 °C), the results are listed in Table 1 and Table 2. CaO was compressed in the same mold at 0.1 Mpa for 10s to ensure consistent test conditions. The results show that the thermal conductivity of CT-15 is increased by approximately 1/3 compared with CaO, which can promote the hydration process.

Table 1 Thermal conductivity of CaO

| Flash point | model | Thermal couductivity (W/m·K) |
| --- | --- | --- |
| 1 | Radiation + pulse on | 0.677 |
| 2 | Radiation + pulse on | 0.725 |
| 3 | Radiation + pulse on | 0.729 |
| Ave | | 0.711 |

Table 2 Thermal conductivity of CT-15

| Flash point | model | Thermal couductivity (W/m·K) |
| --- | --- | --- |
| 1 | Radiation + pulse on | 0.934 |
| 2 | Radiation + pulse on | 0.908 |
| 3 | Radiation + pulse on | 0.922 |
| Ave | | 0.921 |

### 3.3 The cycling test of CT-15

In order to verify the cyclic stability of CT-15, 30 cycles test was carried out in a tube furnace with nitrogen as shielding gas. The dehydration temperature was set at 500 °C (under pure nitrogen) while the hydration temperature was set at 300 °C. The vapor partial pressure during hydration was 45.5 kPa. Fig. 3 shows the schematic diagram of the test system.
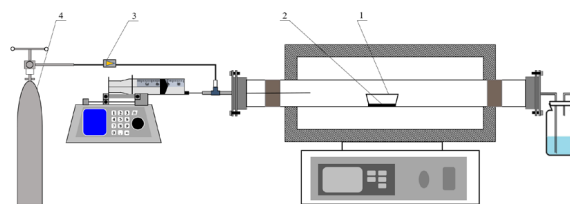

Fig. 3 Cyclic test system diagram
(1- crucible, 2- sample, 3- flow meter, 4- gas cylinder)

Fig. 4 and Fig. 5 show the crushing strength and SEM images of the composite formulation CT-15 with different cycling times. The samples were recompressed every 10 cycles under the same pressure. Furthermore, the exothermic reaction conversion rates of the samples in different cycles were also tested, shown in Fig. 6.

As shown in Fig. 4, although the crushing strength of the composite has decreased, it is still maintained at

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11.73 N after 30 cycles, which is several times greater than the crushing strength of pure CaO. The crushing strength value of 2 N was used as a threshold for judging whether the CaO particles fulfill the mechanical properties requirement of fluidized bed. This threshold has also been adopted in other fluidized-bed applications [15]. Therefore, the composite formulation CT-15 is a suitable candidate for application in $Ca(OH)_2$/CaO based fluidized bed heat storage systems

Moreover, it can be observed in Fig. 5 that the carbon structure still exists after 10 and 30 cycles (Fig. 5 (a) & (b)), the EDS analysis (Fig. 5 (c) & (d)) also indicates that the carbon still exists. That is to say, the matrix carbon has good cycling stability.
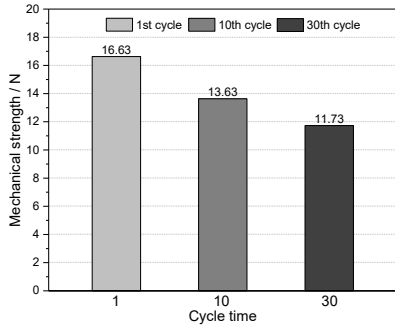

Fig. 4 Crushing strength of CT-15 with different cycles
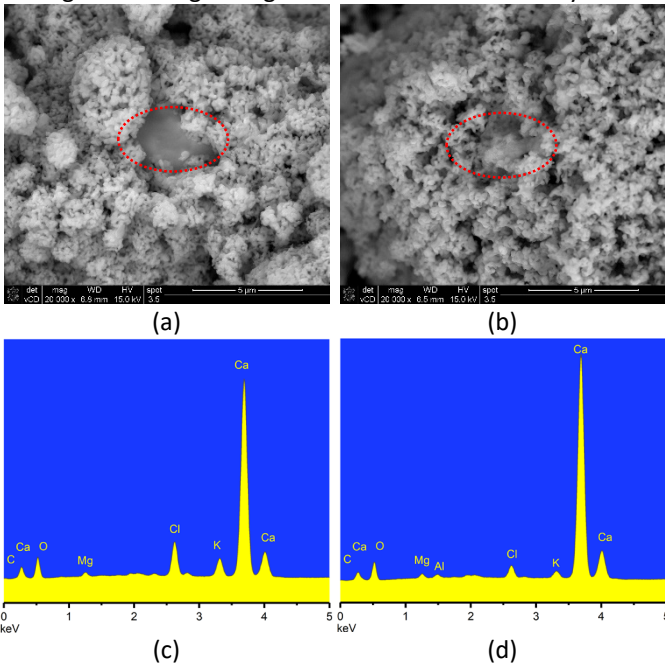


(a)        (b)

(c)        (d)

Fig. 5 SEM images of composite formulation CT-15 with different cycles: (a) 10 cycles (×20000), (b) 30 cycles (×20000), (c,d) EDS analysis (10 cycles left and 30 cycles right)

The exothermic reaction conversion rate can be calculated using Eq. (1).

$$\alpha = \frac{m_{fin} - m_{ini}}{m_{ini} \times w_c} \times \frac{M_c}{M_{H_2O}},$$ (1)

Where, $m_{ini}$ is the initial weight of sample, $m_{fin}$ is the final weight, $w_c$ is the mass ration of CaO, $M_c$ is the molecular weights of CaO while $M_{H_2O}$ is the molecular weight of $H_2O$.

Fig. 6 reveals that in the first ten cycles, CT-15 can be completely converted to $Ca(OH)_2$. As the number of cycles increases, the conversion rate decreases slightly, but it can still be maintained above 90 %, indicating that CT-15 has a good cyclic performance.
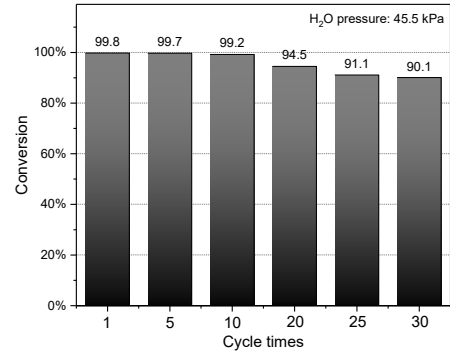

Fig. 6 Conversion rate of CT-15 with different cycles

## 4. CONCLUSIONS

In this study, tar was used as a binder to prepare a composite material with matrix carbon structure as a supporting structure. It is shown that the composite formulation CT-15 has good characteristics for usage in fluidized bed thermochemical energy storage system. The main conclusions are summarized as follows.

- The tar can form a matrix carbon structure under high temperature pyrolysis conditions by adding KCl as the catalyst.
- The matrix carbon structure obtained by tar pyrolysis can provide effective support for CaO particles, thereby reinforcing the mechanical properties. The heat transfer performance of the composite is also improved.
- Due to the low carbon content (10 wt%), the reduction of heat storage density can be acceptable. What's more, the prepared composite has a good cyclic stability.

## 5. ACHNOWLEDGEMENT

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