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# Parameter control in synthesis of Vermiculite-CaCl<sub>2</sub> composite materials for thermochemical adsorption heat storage

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#### ABSTRACT

Keywords: Thermochemical energy storage Thermochemical material Vermiculite Composite material Material characterisation Impregnation method This study utilised vermiculite as a matrix to explore various impregnation methods for synthesising vermiculite-CaCl<sub>2</sub> composite materials (VCMs), focusing on the impact of these methods on the performance of VCMs as thermochemical materials. Results indicate that alternative impregnation methods (e.g., multi-step, vacuum, high pressure, and high temperature) reduce VCM porosity compared to single impregnation, resulting in higher salt content as confirmed by CaCl<sub>2</sub> content tests. Multi-step impregnation yields VCMs with an exceptional salt content of 81.37 wt%, surpassing the highest literature value (68 wt%) and the control group VCM-s (51 wt%). Vacuum impregnation notably increases salt penetration, leading to VCM-vac having the lowest porosity. However, this reduced porosity results in lower hydration and dehydration rates. Notably, VCM-vac exhibits the highest energy storage density of 2.05 GJ/m<sup>3</sup>, which is approximately three times the reported literature values and 1.5 times greater than the study's control group VCM-s. It also exceeds the CaCl<sub>2</sub>-rich VCM-m by 0.2 GJ/m<sup>3</sup>. It also demonstrates superior cyclic stability, with most CaCl<sub>2</sub> remaining internalised, minimising agglomeration and CaCl<sub>2</sub> loss. The energy usage. The findings indicate vacuum impregnation emerges as a preferred method for synthesising thermochemical composite materials.

#### 1. Introduction

Energy storage technology plays an important role in increasing renewable energy generation and enhancing energy security, as it enables the storage of excess energy and later usage when renewable sources are not available [1]. Thermal energy storage (TES) is one type of energy storage, involving the use of a thermal storage medium to store heat [2]. TES can be employed in various applications across different sectors, for instance, buildings (e.g., for heating and cooling), power generation, industrial processes and transportation [3]. The increasing demand for renewable energy sources, such as solar and wind power, is driving the growth of the TES market worldwide. Depending on the type of storage medium, TES systems include sensible heat storage, latent heat storage and thermochemical energy storage (TCES).

Comparatively, TES has gained increasing attention in recent years, owing to its potential for high heat storage density, long-term preservation capability and minimal heat loss during storage [4]. In general, TES operates on the principle of reversible chemical reactions that release or absorb heat. TES is available in a variety of types, and

thermochemical energy storage (TCES) is promising for medium-low temperature applications. TCES may be based on the reversible sorption process between the adsorbent and the adsorbate, with which heat is stored through the endothermic desorption process and is released through the exothermic adsorption process [5,6]. Investigations have been conducted widely for various working pairs of the adsorbent and the adsorbate. Hygroscopic salts are often used as the adsorbents, with water as the adsorbates, such as metal chlorides, bromides and sulfates [7]. Salt hydrates have been preferred for low-temperature heat storage applications, because of their high energy storage densities (400-870  $kWh/m^{3}$ ) and low dehydration temperatures (<150 °C) [8]. A number of candidates for low-temperature heat storage have been reported in the literature, for example, calcium chloride (CaCl<sub>2</sub>) [9], magnesium sulfate (MgSO<sub>4</sub>) [10], magnesium chloride (MgCl<sub>2</sub>) [11], aluminium sulfate (Al<sub>2</sub>SO<sub>4</sub>) [12], sodium sulfide (Na<sub>2</sub>S) [13] and strontium chloride (SrCl<sub>2</sub>) [14]. However, these salts also exhibit certain drawbacks. For instance, the slow kinetics of the hydration reaction in MgSO4 is attributed to the presence of strong hydrogen bonds [15]. Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> necessitates relatively high temperatures for complete dehydration, potentially constraining its applicability in low-temperature energy

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Nomenclature		RV	Raw vermiculite
		SEM	Scanning electron microscope
Symbols		TCES	Thermochemical energy storage
$\Delta H_{ m r}$	Reaction enthalpy, kJ/mol	TCM	Thermochemical material
Μ	Molecular mass, g/mol	TES	Thermal energy storage
т	Mass, g	TGA	Thermogravimetric analysis
n	moles of CaCl <sub>2</sub> in each kilogram sample, mol/kg	VCM	Vermiculite-CaCl <sub>2</sub> composite material
V	Volume, cm <sup>3</sup>	VCM-s	VCM is synthesised via the single impregnation method
w	Water uptake, g/g	VCM-m	VCM is synthesised via the multi-step impregnation
ρ	Density, g/cm <sup>3</sup>		method
$\varphi$	Porosity, %	VCM-vac	VCM is synthesised via the vacuum impregnation method
ω	CaCl <sub>2</sub> content, %	VCM-hp	VCM is synthesised via the high-pressure impregnation
			method
Abbrevia	tions	VCM-htc	VCM is synthesised via the high-temperature
DSC	Differential scanning calorimetry		concentration impregnation method
DRH	Deliquescence relative humidity	VESD	Volumetric energy storage density
ESD	Energy storage density		
GESD	Gravimetric energy storage density		

storage systems [12]. MgCl<sub>2</sub> is prone to hydrolysis as a side reaction. This hydrolysis affects the stability of energy storage systems and generates harmful and corrosive HCl gas [15]. Moreover, Na<sub>2</sub>S reacts with atmospheric carbon dioxide, forming sodium carbonate and releasing hydrogen sulfide gas, which, even in low concentrations, exhibits toxicity [16].

Nevertheless, the employment of pure salt in TCES systems encounters constraints, primarily attributable to its low deliquescence relative humidity (DRH). Once the relative humidity surpasses the DRH threshold, salt hydrates are prone to deliquescence [17]. Salt deliquescence can lead to a reduction in the energy storage capacity and cyclability, agglomeration, corrosion, and degradation of the reactor with increased maintenance requirements [18]. Some studies have demonstrated that salt deliquescence negatively impacts the stability of TCES systems, especially during continuous cycling [19,20]. For example, the potential formation of particle clusters due to salt deliquescence can block the heat transfer channels between the energy storage material and the reactor, consequently resulting in a decrease in the energy storage efficiency.

To mitigate the issue, researchers have investigated composite adsorbent materials, which embed hygroscopic salts in a host matrix with a porous structure (e.g., silica gel [21-23], activated carbon [24-26], zeolites [27-29], vermiculite [30-32], expanded graphite [33–35], silicone foam [36–38], metal-organic frameworks [39–41], carbon/graphene [42-46], pumice [47], mesoporous silica [48], carbonised wood [49], expanded perlite [50], and anodic aluminium oxide [51,52]). The matrix acts as the carrier for immobilising the salts, in which the salts can be distributed uniformly [53]. The high thermal conductivity and porous structure in the host matrix not only significantly enhance the heat and mass transfer performance of thermochemical materials (TCMs) but also promote thermal-chemical cycle stability [54]. For instance, the thermal conductivity of a composite material comprising expanded natural graphite treated with sulfuric acid (ENG-TSA) and SrBr<sub>2</sub> can reach 7.65 W/( $m \cdot K$ ), which is approximately 18 times higher than that of pure SrBr<sub>2</sub> granule salt (i.e., 0.41 W/(m·K)) [55]. Simultaneously, ENG-TSA enhances the permeability of the reaction bed from  $0.7 \times 10^{-12}$  m<sup>2</sup> in its pure state to  $2.7 \times 10^{-12}$  m<sup>2</sup> in the composite state [56]. Furthermore, the incorporation of additional substances, such as silica gel, can prolong the stable cycle number of SrBr<sub>2</sub>-based TCES systems by up to fourfold [57,58].

There are a few methods for synthesising composite materials, and the impregnation method is the most used approach. It involves welldefined steps, offering the ability to synthesise composite materials with high salt loading and good hydrothermal stability [59]. The impregnation methods can be further classified into dry, wet and vacuum impregnation, depending on the operational process [60]. In the impregnation method, the salt hydrate is dissolved in a solvent (i.e., water) producing a salt solution and then drawn into the pores of the host matrix. Dry impregnation, also called incipient wetness impregnation, uses a salt solution whose volume is equal to or slightly lower than the pore volume of the host matrix [61]. Once the host matrix is in contact with the solution, the solution is introduced into the pores by capillary suction, and ideally, no excess crystalline hydrate is observed on the outer surface of the matrix after the drying process. Differently, wet impregnation involves immersing the host matrix in the salt solution, allowing the salt solution to be absorbed into the pores of the host matrix. However, after drying, the excess solution may result in the presence of crystalline salts on the matrix's outer surface, which could potentially cause agglomeration, degradation and instability issues [26]. Unlike the two abovementioned methods, the vacuum impregnation method requires a specialised apparatus that can generate and maintain a certain level of vacuum during the impregnation process [62]. The vacuum impregnation method can achieve a high degree of impregnation, ensuring an even distribution of impregnating substances and minimising issues such as particle agglomeration and surface crystallisation [63].

The energy storage density (ESD) of composite materials largely depends on the salt content, which could be influenced by the impregnation method. Improving the impregnation process can lead to higher salt content in the resulting composite material, thereby enhancing the energy storage capacity and overall performance. Among various methods, the vacuum impregnation technique has demonstrated the ability to achieve salt contents of around 70 wt% within the composite materials [31]. Researchers have also explored the impact of different preparation variables, such as solution concentration, impregnation temperature, and duration, on the resulting composite properties. The concentration of the salt solution has been identified as a critical factor affecting the energy storage performance of the composite material [64]. Additionally, optimisations of the number of impregnation steps [21] and the pressure condition [21] have been carried out to ensure the complete impregnation of the salt solution into the polymer pore spaces, while also preventing the presence of excess solution on the surface of the composite materials.

This study focuses on composites with low charging temperatures (<120 °C) for building applications, and the current research explores the optimization of composite material preparation by controlling various parameters in the impregnation synthesis process. A common combination of host matrix and salt for composite preparation involves

vermiculite and CaCl<sub>2</sub>. Vermiculite, a naturally non-toxic mineral, finds extensive applications in fields such as construction and horticulture due to its lightweight, chemical inertness, flame retardancy, and odourless characteristics, making it a popular choice as the main host matrix for composite materials [55]. Researchers have shown keen interest in CaCl<sub>2</sub> for several reasons. Firstly, CaCl<sub>2</sub> is readily obtainable and relatively economically affordable (less than  $0.4 \notin /kg$ ). Secondly, it exhibits excellent water absorption capacity and ESD, demonstrating outstanding energy storage potential. Furthermore, compared to other salt hydrates, CaCl<sub>2</sub> possesses superior chemical stability, low corrosiveness, and non-toxic properties. Of particular significance is its ability to undergo dehydration reactions at relatively low temperatures (below 100 °C), making it highly suitable for low-temperature energy storage applications [65]. These combined factors render CaCl<sub>2</sub> a highly promising salt hydrate, particularly suitable for various applications in building-related TCES. The reversible chemical gas-solid reactions involving dehydration and hydration reactions are expressed below:

The dehydration process of calcium chloride hexahydrate into anhydrous calcium chloride does not occur in a single step; instead, it takes place in multiple stages [66]. The known dehydration and hydration steps of calcium chloride along with their reaction enthalpies are listed in Table 1 [67].

Currently, there are three different methods for preparing vermiculite-CaCl<sub>2</sub> composite materials. One method involves slowly adding a saturated CaCl<sub>2</sub> solution to vermiculite while continuously stirring until complete wetting is achieved [68]. Another method entails continuously spraying a saturated CaCl<sub>2</sub> solution onto vermiculite while stirring slowly to prepare the composite material [69]. The third method involves periodically spraying a saturated CaCl<sub>2</sub> solution onto a fixed quantity of vermiculite until all the solution is absorbed by the vermiculite [70]. Studies have indicated that the optimal mass mixing ratio of vermiculite to CaCl<sub>2</sub> is 2:1, and no excess salt crystals appear on the surface of the composite material. However, the results regarding comprehensive material performance, especially concerning structural properties and salt loading percentages, are still limited.

This study synthesised vermiculite-CaCl<sub>2</sub> composite materials using traditional single impregnation and four updated methods, with the former serving as the control group. To comprehensively assess the performance and effects of the resultant composite materials, various characterization techniques were employed to evaluate their properties (e.g., structural characteristics, CaCl<sub>2</sub> content, hydration and dehydration capacities, energy storage density, cyclic stability, and energy consumption during synthesis). Based on reported results in the literature, the vermiculite-CaCl<sub>2</sub> composite achieved a slate content of 68 wt % through a single-step impregnation method, with an ESD of 0.5 GJ/m<sup>3</sup> [65]. The data presented in the references and the performance parameters of the control group in this study serve as reference points for result analysis. This allows for the evaluation of the impact of impregnation parameters (e.g., temperature and concentration of the CaCl<sub>2</sub> solution, number of impregnation steps, and impregnation pressure) on the properties of the resulting composite materials. These findings offer valuable insights into effective impregnation methods for synthesising performance-enhanced composite materials, potentially paving the way

#### Table 1

The dehydration and hydration steps of  $\mbox{CaCl}_2$  hydrates with their reaction enthalpies.

Reaction	$\Delta H_{\rm r}$ (kJ/mol)
$CaCl_2 \cdot 6H_2O + \Delta H_r \leftrightarrow CaCl_2 \cdot 4H_2O + 2H_2O$	120.7
$CaCl_2 \cdot 4H_2O + \Delta H_r \leftrightarrow CaCl_2 \cdot 2H_2O + 2H_2O$	117.1
$CaCl_2 \cdot 2H_2O + \Delta H_r \leftrightarrow CaCl_2 \cdot 1H_2O + 1H_2O$	51.9
$CaCl_2 \cdot H_2O + \Delta H_r \leftrightarrow CaCl_2 + H_2O$	71.6

for novel approaches in developing more efficient low-grade thermochemical adsorption heat storage systems for building applications.

# 2. Different approaches for synthesising Vermiculite-CaCl<sub>2</sub> composite material

In this study, five types of vermiculite-CaCl<sub>2</sub> composite materials (referred to as VCM) have been synthesised using various impregnation methods. These include the conventional single impregnation method (VCM-s), multi-step impregnation technique (VCM-m), vacuum impregnation method (VCM-vac), high-pressure impregnation method (VCM-hp), and high-temperature concentration impregnation method (VCM-hc). The latter four methods are proposed based on the conventional single impregnation method by refining various synthesis parameters (e.g., the impregnation step, impregnation pressure, temperature, and concentration ratio of aqueous solutions). Fig. 1 illustrates the sequential synthesis steps of the five impregnation methods. Vermiculite was sourced from Fisher Scientific UK Ltd, and anhydrous CaCl<sub>2</sub> was procured from Merck Life Science UK Ltd. The detailed descriptions of the specific procedural steps of the five impregnation methods are listed below:

Conventional single impregnation method:

- (1) Dry raw vermiculite in an oven (Fig. 2a), set at 150  $^{\circ}$ C for 24 h, ensuring thorough desiccation, followed by allowing the vermiculite to cool to room temperature.
- (2) Place 100 g fully dried vermiculite into a container and submerge it completely with saturated CaCl2 solution. Ensure the vermiculite remains completely immersed for 1 h.
- (3) Transfer the wet composite material to a filter to remove excess saturated solution. Subsequently, dry it in a 150  $^{\circ}$ C oven for 24 h to ensure complete dehydration.

Multi-step impregnation method:

- Same as the steps 1–3 of the conventional single impregnation method.
- (2) Iteratively repeat steps 2 and 3 until the composite material achieves the desired salt content.

Vacuum impregnation method:

- (1) Same as step (1) of the conventional single impregnation method.
- (2) Place the completely dried vermiculite 100 g into a vacuum chamber (Fig. 2d) and employ a vacuum pump to extract air until the pressure inside reaches 10 kPa.
- (3) Close the vacuum pump valve and open the valve leading to the solution. Due to the pressure differential, the saturated CaCl<sub>2</sub> solution is drawn into the chamber.
- (4) Close the valve once the vermiculite is completely submerged in the saturated CaCl<sub>2</sub> solution. Maintain immersion for 1 h.
- (5) Same as step (3) of the conventional single impregnation method.

High-pressure impregnation method:

- (1) Same as step (1) of the conventional single impregnation method.
- (2) Place 100 g of completely dried vermiculite into a high-pressure chamber (Fig. 2b), then pour saturated calcium chloride solution into the chamber until the material is fully submerged.
- (3) Subsequently, pressurize the chamber to 2 atm and maintain this pressure for 1 h.
- (4) Same as step (3) of the conventional single impregnation method.

High-temperature high concentration impregnation method:

(1) Same as step (1) of the conventional single impregnation method.



Fig. 1. Illustration of synthesis steps for five impregnation methods.

- (2) Utilise the heating function within a hot stirrer (Fig. 2c) to increase the water temperature in a beaker to 80  $^{\circ}$ C.
- (3) Gradually introduce anhydrous CaCl<sub>2</sub> into the heated water at a mass 1.4 times that of the water. Ensure continuous and thorough stirring until complete dissolution occurs, yielding a concentrated CaCl<sub>2</sub> solution with a weight concentration of 58 %.
- (4) Sustain constant heating throughout the dissolution process to keep the solution temperature above 80 °C, preventing the precipitation of CaCl<sub>2</sub> crystals.
- (5) Immerse the completely dried vermiculite (100 g) in this hightemperature concentrated solution, allowing it to remain immersed for 1 h.
- (6) Same as step (3) of the conventional single impregnation method.

#### 3. Characterisation of Vermiculite-CaCl<sub>2</sub> composite materials

Five VCM samples were prepared using the aforementioned methods and characterised via various techniques to assess the impact of synthesis parameters on composite material performance. Firstly, scanning electron microscopy (SEM) was employed to provide insights into the composites' microstructure, revealing surface morphology and internal constitution. The mercury intrusion porosimetry (MIP) was utilised to outline the pore structure, providing results of pore volume and size distribution. Additionally, the inductively coupled plasma optical emission spectroscopy (ICP-OES) method was employed to precisely analyse the respective salt content within each VCM sample.

#### 3.1. Scanning electron microscope analysis

Using the Philips (FEI) XL30 scanning electron microscope (SEM),

we conducted observations of the morphology and microstructure of various synthesised vermiculite-CaCl<sub>2</sub> composite materials. The original vermiculite exhibited axial lengths ranging from 3 to 10 mm and cross-sectional areas of 0.64–2 cm<sup>3</sup>. Initially, vermiculite displayed a highly porous nature, forming a stacked thin-layered structure as shown in Fig. 3a.

In the VCM-s sample, the distinct laminar structure of vermiculite remained visible, yet  $CaCl_2$  was coated onto the layer surfaces and filled interlayer spaces (Fig. 3b). In contrast, the enhanced preparation methods for VCM-m, VCM-vac, VCM-hp, and VCM-htc exhibited notably different morphologies, particularly VCM-m (Fig. 3c). In VCM-m, the salt almost completely occupied the interlayer spaces of the vermiculite, obscuring the original layered structure. However, pore-like structures appeared on the surface of VCM-m. This phenomenon is due to the presence of air within vermiculite's pores. When the salt solution was directly impregnated into the vermiculite, the air became confined and underwent compression within the smaller and narrower pores. During the drying process, these gases expand and break through the surface created by salt, forming these small pores. A similar phenomenon was noted in both VCM-hp (Fig. 3e) and VCM-htc (Fig. 3f).

Differently, VCM-vac (Fig. 3d), which was prepared using the vacuum impregnation method, did not display a notable presence of pore structures on its final surface. This is because of the removal of a substantial portion of the air from within the vermiculite before impregnation, which facilitates increased salt impregnation into the pores of vermiculite without air hindrance. Similar to VCM-s, VCM-hp (Fig. 2e) maintained the layered structure of vermiculite, but a noticeable accumulation of salt was observed on its surface. In VCM-htc (Fig. 3f), although the outline of the original layered structure remained visible, it's important to note that most of the interlayer spaces had been



Fig. 2. Instruments used in the synthesis of VCMs: (a) Oven; (b) High pressure chamber; (c) Hot stirrer; and (d) Vacuum chamber with pump.

occupied with salt.

#### 3.2. Pore structure characterisation and density analysis

In this study, the pore structures of RV and five VCMs were examined with the Micromeritics Autopore IV 9500 instrument using the MIP technique. To ensure the analysis accuracy, all samples were thoroughly dried prior to the MIP characterisation to eliminate any residual moisture that might have been absorbed during storage. Subsequently, the samples were cooled to room temperature. During the testing phase, samples were initially immersed in a mercury environment, and pressure was applied to facilitate mercury infiltration into the sample's pores. The gradual increase in pressure induces changes in the mercury infiltration into the sample's pores, and the recording of mercury intrusion quantities at different pressures allows for the derivation of pore size distributions. Simultaneously, determining the sample's total volume and pore volume (total mercury intrusion volume) was accomplished by measuring the displacement of mercury and the resulting volume changes.

Fig. 4 presents the pore structure distributions of the RV and the five VCMs. The peak of each curve represents the pore size that appears with the highest frequency in the material's pore size distribution. The results

indicate that all six samples have minimal pore sizes above 0.1 µm, confirming their classification as macro-porous structures. The peak distribution for the untreated vermiculite falls within the range of 1 and 10  $\mu$ m, which is similar to the pore structure distribution observed in VCM-htc. VCM-m displays a broader range of pore sizes spanning from 1000 to 100000 nm, without a prominent peak. Notably, the pore structure distributions of both VCM-s and VCM-hp primarily centre between 10 and 100 µm, indicating an enlargement of pore sizes compared to the RV. This expansion is attributed to the salt swelling within the vermiculite's pores during the drying process, causing the remaining pores to expand. Conversely, VCM-vac, which was prepared using the vacuum impregnation method, exhibits a pore range distribution ranging from 0.1 to 1  $\mu$ m, with few pores exceeding 1  $\mu$ m. It is due to the vacuum evacuation of air within the vermiculite prior to impregnation, enabling a more efficient impregnation of salt into the pores.

The detailed pore parameter results for all samples are provided in Fig. 5. Because of the impregnation with salt, VCMs demonstrate a significant decrease in both porosity and total mercury intrusion volume (i. e., pore volume) compared to RV, confirming the pores are filled with CaCl<sub>2</sub>. The porosity of VCM-s and VCM-hp remains consistent at approximately 70 %, which is about 12 % points lower than that of RV.



Fig. 3. SEM photos of (a) RV, (b) VCM-s, (c) VCM-m, (d) VCM-vac, (e) VCM-hp, and (f) VCM-htc.



Fig. 4. Pore size distribution of RV and five VCMs using the MIP technique.

VCM-m and VCM-htc, synthesised using the multi-step impregnation method and the high-pressure high-temperature concentration impregnation method, exhibit porosities of 60.75 % and 65.97 %, respectively. This marks a significant decrease of approximately 20 % points compared to RV's porosity. As the vacuum impregnation process eliminates residual air hindrance within pores, VCM-vac exhibits the lowest porosity at 50.11 %. This represents a substantial reduction of over 30 % points from the RV's porosity, indicating the remarkable effectiveness of vacuum impregnation in fully achieving salt impregnation within the vermiculite's pores. In line with porosity, the total mercury intrusion volume (pore volume) of the samples follows a similar trend.

Furthermore, as depicted in Fig. 5, the average pore diameters of VCM-s and VCM-hp exceed that of RV, measuring approximately  $3.8 \,\mu$ m and  $3.2 \,\mu$ m, respectively. This expansion results from the swelling of salt within the pores during the drying process. However, VCM-m, VCM-vac, and VCM-htc display average pore diameters smaller than that of RV, particularly VCM-m and VCM-vac, with average pore diameters of only 0.25 and 0.39  $\mu$ m, respectively. This reduction is attributed to an

increased filling of salt within the vermiculite pores.

Based on the total mass, total volume and pore volume of the sample obtained from the aforementioned tests, the density of the sample can be computed. Bulk density represents the ratio of the total mass of the sample to its total volume, and it can be calculated using the following equation:

$$\rho_{\text{bulk}} = \frac{m_{\text{VCM}}}{V_{\text{VCM}}} \tag{2}$$

where  $m_{\text{VCM}}$  is the total mass of the dried VCM sample, g;  $V_{\text{VCM}}$  is the total volume of the dried VCM sample, cm<sup>3</sup>.

The apparent density of particles considers the presence of pores within the sample, representing the ratio of the total mass to the volume effectively occupied by the particles. The calculation equation is as follows:

$$\rho_{\text{apparent}} = \frac{m_{\text{VCM}}}{V_{\text{VCM}} - V_{pore}} = \frac{m_{\text{VCM}}}{V_{\text{VCM}}(1 - \varphi)} \tag{3}$$

where  $V_{\rm pore}$  is the pore volume of the VCM,  ${\rm cm}^3; \varphi$  is the porosity of the VCM.

The bulk and apparent densities of RV and five VCMs were analysed using the MIP technique, and results are presented in Fig. 6. All VCMs show noticeable increases in the bulk density compared to the RV, particularly VCM-vac with a bulk density of 0.88 g/cm<sup>3</sup>, almost four times that of RV. This increase can be attributed to the denser nature of calcium chloride. When integrated with the lightweight vermiculite, it leads to an overall greater mass and consequently contributes to a higher bulk density of the composite. Furthermore, the vacuum impregnation method prevented the formation of sealed voids caused by residual air in VCM-vac. The apparent density of all five VCMs has increased compared to RV. Among them, the apparent density of VCM-m has shown the most significant increase, rising by 0.25 g/cm<sup>3</sup> to reach 1.78 g/cm<sup>3</sup> when compared to RV.

#### 3.3. Salt content analysis

Three different techniques have been employed for quantifying the salt content within the five VCMs, including Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), weighing analysis, and pore volume analysis. The results of the CaCl<sub>2</sub> content for the five VCMs are shown in Fig. 7. ICP-OES involves the determination of CaCl<sub>2</sub> content



Fig. 5. Pore parameter results for RV and five VCM samples.



within a VCM through the measurement of the mass ratio of the VCM and calcium. For VCM-s, which was synthesised using the conventional single impregnation method, the CaCl<sub>2</sub> content is 51.36 wt%. Noticeable improvements in the CaCl<sub>2</sub> content are observed in VCM-m, VCM-vac, VCM-hp, and VCM-htc. Notably, VCM-m exhibits the highest CaCl<sub>2</sub> content, reaching 81.37 wt%. The CaCl<sub>2</sub> content in VCM-vac is 71.08 wt %, approximately 10 % points lower than VCM-m, and slightly less than VCM-htc (i.e., 72.16 wt%). Despite the findings from Sections 3.1 and 3.2 indicating that VCM-vac contains the highest CaCl<sub>2</sub> contents within its pores, both VCM-m and VCM-htc exhibit a substantial salt presence on their exterior surfaces as observed in Fig. 3. This phenomenon contributes to the higher final CaCl<sub>2</sub> content in VCM-m and VCM-htc in comparison to VCM-vac. Meanwhile, the CaCl<sub>2</sub> content in VCM-hp (i.e., 61.86 wt%) indicates a modest increase of approximately 10 % points compared to VCM-s.

Additionally, there exist two alternative methods for the rapid determination of CaCl<sub>2</sub> content within VCM samples. One method involves weighting analysis, wherein the difference in mass between the dried VCM samples and the initial mass of vermiculite is utilised to



Fig. 7. CaCl<sub>2</sub> content in five VCM samples using three techniques.

calculate the CaCl<sub>2</sub> content. The calculation equation is as follows:

$$\omega = \frac{m_{\rm VCM} - m_{\rm v}}{m_{\rm VCM}} \tag{4}$$

where  $m_{\text{VCM}}$  is the total mass of the dried VCM sample, g; and  $m_{\text{v}}$  is the mass of the initial mass of the vermiculite, g.

The CaCl<sub>2</sub> content in VCM samples calculated through weighting analysis is slightly lower than that obtained via ICP-OES analysis. This disparity may be attributed to potential mass losses inherent in the synthesis and transfer processes. Another method entails the determination of CaCl<sub>2</sub> content within the VCM sample by analysing the bulk density of both the VCM sample and raw vermiculite, as expressed by the following equation:

$$\omega = \frac{\rho_{\text{bulk,VCM}} - \rho_{\text{bulk,VCM}}}{\rho_{\text{bulk,VCM}}} \tag{5}$$

where  $\rho_{\text{bulk,VCM}}$  is the bulk density of VCM sample, g; and  $\rho_{\text{bulk,v}}$  is the bulk density of the raw vermiculite, g.

However, the CaCl<sub>2</sub> content of VCM samples calculated via bulk density measurements tends to be lower compared to the results obtained through ICP-OES analysis. This deviation might stem from the potential blockage of some small pores during the preparation of VCM samples, hindering the infiltration of CaCl<sub>2</sub> solution, consequently leading to underestimated bulk density measurements, and affecting the accuracy of the calculations.

#### 3.4. Sorption performance analysis

This study assessed the hydration levels of CaCl<sub>2</sub> within VCMs and the water uptake of VCMs in the hydration process. Initially, the five VCM samples underwent a 24-h dehydration process at 150 °C in an oven to ensure complete dehydration. Afterwards, the samples were cooled to 20 °C using a freeze-drying apparatus and then transferred to a high-precision environmental chamber (Genlab multifunctional benchtop incubator) equipped with accurate weighing scales for experimentation. To ensure consistent and thorough penetration, the samples were arranged on precise weighing scale trays and evenly spread into thin layers for testing. The environmental chamber maintained a constant temperature of 20 °C, while the relative humidity was set at 30 %, 50 %, and 70 % for continuous testing periods of 12 h respectively.

The hydration level of salts within VCMs is determined as follows:

hydration level = 
$$\frac{n_{\rm H_2O,ab}}{n_{\rm CaCl_2}} = \frac{\left(m_{\rm VCM,i} - m_{\rm VCM}\right)/M_{\rm H_2O}}{\omega m_{\rm VCM}/M_{\rm CaCl_2}}$$
(6)

where  $n_{\rm H_2O,ad}$  represents the number of moles of water adsorbed, mol;  $n_{\rm CaCl_2}$  signifies the number of moles of CaCl<sub>2</sub> in VCMs, mol;  $m_{\rm VCM,i}$  stands for the mass of VCMs during the hydration process, g;  $M_{\rm H_2O}$  represents the molar mass of water, g;  $M_{\rm CaCl_2}$  and denotes the molar mass of calcium chloride, g.

The water uptake performance is determined as follows:

$$w = \frac{m_{\rm VCM,i} - m_{\rm VCM}}{m_{\rm VCM}} \tag{7}$$

The CaCl<sub>2</sub> hydration levels and water absorption rates of five types of VCMs, pure CaCl<sub>2</sub>, and raw vermiculite at different relative humidity conditions are illustrated in Fig. 8. As depicted in Fig. 8, the hydration levels of CaCl<sub>2</sub> in VCM increase with both the relative humidity of their surrounding environment and their own porosity. This escalation is due to the heightened contact between the moisture molecules in the air and CaCl<sub>2</sub> within VCM, prompted by higher relative humidity and porosity.



Fig. 8. Sorption kinetics of the RV and five VCM samples at 20 °C and various relative humidity levels (30 %, 50 % and 70 %).

Specifically, at a relative humidity of 30 %, the hydration levels of CaCl<sub>2</sub> in the five types of VCM are arranged according to their respective porosity, ranging around 1.8–1.9 mol/mol. Upon an increase in relative humidity to 50 %, the ranking of CaCl<sub>2</sub> hydration levels among the five types of VCM remains consistent and is concentrated around 4–8 mol/ mol. VCM-s and VCM-hp have higher hydration levels of CaCl<sub>2</sub> and exhibit deliquescence, with their CaCl<sub>2</sub> hydration levels positioned at approximately 6 mol/mol and 8 mol/mol, respectively. At a relative humidity of 70 %, the arrangement of CaCl<sub>2</sub> hydration levels among the five types of VCM continues to be determined by their porosity, with all VCMs showcasing CaCl<sub>2</sub> hydration levels surpassing 7 mol/mol, displaying deliquescence phenomena.

At a relative humidity of 30 %, pure CaCl<sub>2</sub> exhibits hydration levels close to those of VCM-vac, and lower than the hydration levels of the other four VCMs, owing to the inherent porous nature of VCMs. This porous structure enables an expanded contact surface area between moist air and the internal CaCl<sub>2</sub> within VCMs. However, at a relative humidity of 50 %, VCMs with lower porosity (e.g., VCM-m, VCM-vac, and VCM-htc) experience lower hydration levels compared to pure CaCl<sub>2</sub>. This discrepancy arises due to the expansion of salt hydrates within the smaller pore structure of VCMs during increased relative

humidity, resulting in partial blockage of smaller pores that impede the ingress of moist air. As the relative humidity escalates to 70 %, the hydration level of pure  $CaCl_2$  once again records the lowest value compared to the five types of VCM. This difference emerges because calcium chloride might have reached its maximum moisture absorption capacity at a relative humidity of 50 %. As depicted in the graph, the hydration level of pure CaCl<sub>2</sub> remains consistently around 6 mol/mol as the surrounding relative humidity increases from 50 % to 70 %.

Among the five VCMs, VCM-vac showcases the least effective water absorption performance across three distinct relative humidity levels due to its low porosity, consequently affecting the hydration levels of CaCl<sub>2</sub> in VCM-vac. Despite VCM-s having the lowest CaCl<sub>2</sub> content among the five VCM types, it demonstrates the highest water absorption capabilities at 30 %RH and 50 %RH, with respective water absorption rates of 0.26 g/g and 0.67 g/g. However, under high humidity testing conditions (i.e., 70 %RH), the water absorption rate of VCM-s is eventually exceeded by VCM-m and VCM-htc, reaching a final value of 1.04 g/g. This shift can be attributed to the lower content of CaCl<sub>2</sub> in VCM-s. Despite reaching a hydration level near 12 mol/mol, its water absorption rate remains lower compared to VCM-m and VCM-htc, both containing higher amounts of CaCl<sub>2</sub>. RV exhibits the weakest water



Fig. 9. Desorption kinetics of the RV and five VCM samples at various temperatures (90 °C, 120 °C and 70 °C).

absorption performance, consistently maintaining a rate below 0.1 across the three different relative humidity tests.

#### 3.5. Desorption performance analysis

This section evaluates the hydration levels of CaCl<sub>2</sub> in five VCMs and their mass loss during the dehydration process. Prior to commencing the study, five types of VCMs were subjected to a hydration treatment in an environmental chamber maintained at 20 °C and relative humidity of 50 %, until the CaCl<sub>2</sub> in the VCMs attained a water molecule loading of 6 mol/mol. Subsequently, the chamber's temperature was set to 90 °C, 120 °C, and 150 °C for dehydration testing respectively. The mass of the VCMs was recorded using high-precision scales within the chamber. The dynamic hydration levels of CaCl<sub>2</sub> in VCMs and the dynamic residual weights of VCMs are presented in Fig. 9.

The decline degree and rate of CaCl<sub>2</sub> hydration level in five different VCMs under three distinct temperature conditions (i.e., 90 °C, 120 °C, and 150 °C) are directly associated with the porosity of the VCMs. VCMs characterised by a higher porosity exhibit a more pronounced reduction in hydration levels and a faster reduction rate (i.e., a higher dehydration reaction rate) during the dehydration process. This phenomenon arises from the larger internal pore surface area present in VCMs with higher porosity, which facilitates greater accessibility of high-temperature air to the CaCl<sub>2</sub> encapsulated within the pores. Consequently, this expedites the dehydration reaction. For instance, under the 150 °C condition, the CaCl<sub>2</sub> within the VCM with the highest porosity has completed full dehydration within 100 min, while in VCMs with larger porosities, the hydration level of CaCl<sub>2</sub> remains at 0.5 mol/mol even after 180 min. With the increasing ambient temperature, both the extent and rate of CaCl<sub>2</sub> hydration reduction within VCMs demonstrate an augmentation. Specifically, within the same reaction duration, at 90 °C, the final hydration levels of the five VCMs range between 2.5 and 4.0 mol/mol, decreasing to 0.5-1.5 mol/mol at 120 °C. At 150 °C, the majority of CaCl<sub>2</sub> hydrates within the VCMs have essentially completed the dehydration process.

Comparatively, VCM-s and VCM-hp exhibited the most significant final weight loss at 90 °C, attributable to their elevated porosity levels, with respective weight losses of 19.63 % and 19.83 % over the dehydration process. This trend, however, was reversed at higher temperatures. At 120 °C, the final weight losses of VCM-s and VCM-hp were surpassed by VCM-m and VCM-htc, and at 150 °C, even the least porous VCM-vac exceeded their weight loss. This shift is linked to the relatively lower CaCl<sub>2</sub> content in VCM-s and VCM-hp. At 120 °C and 150 °C, the CaCl<sub>2</sub> hydrates in all five VCMs were either in the final stages of dehydration or almost completely dehydrated. During this phase, the differences in the hydration levels of CaCl<sub>2</sub> within the VCMs became smaller. Consequently, VCMs with higher CaCl<sub>2</sub> content, namely VCM-m, VCM-vac, and VCM-htc, achieved greater final weight loss than VCM-s and VCM-hp.

#### 3.6. Energy storage density analysis

The differential scanning calorimetry (DSC) system TA SDT-Q650 was employed in this study to evaluate the energy storage density (ESD) of CaCl<sub>2</sub>·6H<sub>2</sub>O and five types of VCMs. Prior to testing, the dried VCMs were placed in a temperature and humidity-controlled chamber, maintaining a temperature of 20 °C and a relative humidity of 50 % for 12 h to acquire hydrated VCMs. Subsequently, the CaCl<sub>2</sub>·6H<sub>2</sub>O and the five hydrated VCMs were placed into the TA SDT-Q650, and measurements were conducted under a nitrogen flow, ramping from 30 °C to 150 °C at a heating rate of 1 °C/min. The TA SDT-Q650 device was used to track the desorption (hydration) process of CaCl<sub>2</sub>·6H<sub>2</sub>O and hydrated VCM as the temperature increased, a process accompanied by endothermic phenomena. By analysing changes in the thermal energy of nitrogen, the enthalpy values (gravimetric energy storage density, GESD) of the CaCl<sub>2</sub> and hydrated VCM samples were obtained.

The ESD is a crucial parameter, as a TCM with superior energy density contributes to a more compact and efficient TCES system. ESD can be derived from the heat flow in the DSC measurement. The theoretical GESD is determined using Eq. (8).

$$ESD = n \cdot \Delta H_{\rm r} \tag{8}$$

where *n* is moles of CaCl<sub>2</sub>·6H<sub>2</sub>O in each kilogram sample, mol/kg;  $\Delta H_r$  is the hydration enthalpy of CaCl<sub>2</sub>·H<sub>2</sub>O, kJ/mol [65].

Fig. 10 presents the GESD and volumetric energy density (VESD) of dry VCM particles obtained through actual measurements via DSC and theoretical calculations for pure CaCl<sub>2</sub> and the five types of VCM. The GESD of pure CaCl<sub>2</sub> in the test sample is the highest among the samples tested, reaching 3221.44 kJ/kg. This value is relatively close to the data reported in the literature (i.e., 3330 kJ/kg) [66] and the values obtained through theoretical calculations. The observed disparity between these values might stem from a minor pre-testing dehydration of the examined CaCl<sub>2</sub> sample.

The GESD of VCMs shows a positive correlation with their CaCl<sub>2</sub> content, where higher salt content corresponds to greater ESD, a trend supported by theoretical values depicted in the graph. The theoretically calculated GESD for VCMs synthesised using alternative methods exceeds that of conventionally produced VCM-s through dry impregnation. However, in actual testing, despite VCM-s and VCM-hp having the lowest CaCl<sub>2</sub> content among the five VCMs, their GESD are the highest, and surpassing theoretical predictions to reach 2231.67 kJ/kg and 2067.75 kJ/kg, respectively. This peculiarity arises from the hydration levels of CaCl<sub>2</sub> within VCM-s and VCM-hp during VCM hydrate creation, surpassing 6 mol/mol (the state of CaCl<sub>2</sub>·6H<sub>2</sub>O). Besides the heat absorption due to the dehydration reaction of CaCl<sub>2</sub>, there is additional heat absorption from extra water molecules evaporating during DSC testing. Conversely, the GESDs of VCM-m, VCM-vac, and VCM-htc, which possess higher CaCl<sub>2</sub> content, fall below the theoretical values. This discrepancy arises from their slower absorption rates. Despite employing a similar timeframe and environment for VCM hydrate preparation as VCM-s and VCM-hp, they did not reach the 6 mol/mol threshold (i.e., the CaCl<sub>2</sub>·6H<sub>2</sub>O state).

In terms of building applications, the compact integration of diverse equipment and systems within confined spaces emphasises the critical focus on the VESD of storage materials. Among the five VCMs, VCM-vac demonstrates the lowest measured GESD. However, its measured VESD closely aligns with that of VCM-m, hovering around 1.4 GJ/m<sup>3</sup>, surpassing VCM-htc with similar CaCl<sub>2</sub> content. Notably, the theoretical volumetric ESD of VCM-vac reaches 2.1 GJ/m<sup>3</sup>, standing as the highest among all VCMs, even surpassing VCM-m, which contains the highest CaCl<sub>2</sub> content. This outcome results from employing multiple immersion methods and high-temperature, high-concentration method leading to increased particle volume in VCM-m and VCM-htc, subsequently reducing their bulk density.

Comparatively, VCMs synthesised through different impregnation methods exhibit more pronounced enhancements in volumetric energy density than GESD, VCM-m and VCM-vac showing an approximate 40 % increase in measured VESD compared to VCM-s. Furthermore, the theoretical VESD of VCM-vac doubles that of VCM-s.

#### 3.7. Cyclability analysis

When evaluating the cyclic stability of TCMs, two crucial criteria are water uptake and weight retention rate. To obtain data closer to real-world applications, the five VCMs were individually placed in small-scale packed beds and then collectively positioned in a TCES reactor for discharging (hydration) testing. During the discharging test, the inlet conditions were set at a constant temperature of 20 °C and a relative humidity of 40 %, maintained for a duration of 3 h. Throughout the period, air flowed through the VCMs at a velocity of 0.5 m/s. The charging (dehydration) process was conducted in an oven at 150 °C for



Fig. 10. (a) The measured and theoretical GESD (based on particle) for CaCl<sub>2</sub> and five VCMs; (b) The measured and theoretical VESD (based on particle) for CaCl<sub>2</sub> and five VCMs.

24 h, ensuring complete drying of the VCMs. The discharging and charging cycles were repeated 20 times to simulate the cyclic usage in real applications. The water absorption capacity was assessed in each cycle by comparing the mass increase after the discharge process to that of the fully dried samples, while the weight retention rate was determined by calculating the percentage of mass retained after each charging process compared to the initial sample mass.

Fig. 11 presents the water absorption capacity of the five VCMs in each cycle. Compared to VCM-s, synthesised using the conventional single impregnation method, the other four VCMs showed a greater decline in water absorption capacity after 20 cycles. Particularly, VCMm exhibited a 13.00 % decrease in water absorption capacity in the 20th cycle compared to the initial cycle. This decline was nearly 5 % points greater than that of VCM-s. This is primarily due to significant clumping resulting from the abundant presence of CaCl<sub>2</sub> on the VCM-m surface. The water absorption capacities of the other three VCMs decreased by approximately 0.5–1.5 % points compared to VCM-s.

Table 2 lists the weight retention rates of the five VCMs in the 1st, 5th, 10th, 15th and 20th cycles. VCM-vac demonstrated the lowest mass loss (i.e., only 0.37 %) over 20 cycles. This is attributed to most of its CaCl<sub>2</sub> being concentrated in internal pores, making it less prone to escape. In contrast, VCM-hp showed a higher mass loss, exceeding 1 % in the first cycle. Overall, although the water absorption capacity loss of VCM-vac is slightly higher than that of VCM-s, the difference is minimal. Additionally, VCM-vac exhibited the lowest weight loss, indicating its higher stability in cyclic usage.



 Table 2

 Weight retention rates of five VCMs in different cycles.

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Number of cycles	VCM-s	VCM-m	VCM-vac	VCM-hp	VCM-htc
1	99.80 %	99.94 %	100.00 %	98.96 %	99.94 %
5	99.60 %	99.88 %	100.00 %	98.89 %	99.77 %
10	99.53 %	99.88 %	99.90 %	98.82 %	99.65 %
15	99.53 %	99.75 %	99.81 %	98.75 %	99.54 %
20	99.46 %	99.61 %	99.63 %	98.75 %	99.42 %

#### 3.8. Discussions

Kinetic rate, energy density, and cycling stability stand as the most crucial indicators for any TCM in a TCES system. However, achieving the pinnacle in all three parameters simultaneously poses a significant challenge. During the charging and discharging processes, the rate of hydration/dehydration reactions of the five types of VCMs exhibited consistency. The speed of these reaction rates primarily depended on the porosity of each VCM, with VCMs having higher porosity exhibiting faster rates of hydration (discharging) and dehydration (charging). Among these five VCMs, VCM-s showed the fastest reaction rate, while VCM-vac displayed the slowest reaction rate. However, VCM-vac exhibited the highest volumetric energy density (based on particle) among five VCMs, reaching 2.05 GJ/m<sup>3</sup>. This value is nearly 1.5 times higher compared to the control group VCM-s in this study and even exceeds that of VCM-m, which has the highest CaCl2 content, by 0.2 GJ/ m<sup>3</sup>. Simultaneously, VCM-vac exhibits optimal cycling stability due to most CaCl<sub>2</sub> being situated within VCM-vac rather than on the surface, preventing particle agglomeration during reactions and minimising CaCl<sub>2</sub> loss within the pores.

Concerning future TCM widespread applications, the energy consumption required for synthesising each kilogram of dry CaCl<sub>2</sub> into vermiculite during VCM synthesis is a noteworthy consideration. According to Table 3, VCM-s displays an energy consumption of 2.93 kWh/ kg. However, the energy consumption of VCMs synthesised using four other methods increases due to the additional processing steps. Nonetheless, VCM-vac demonstrates the closest energy consumption, being approximately only 0.55 kWh/kg higher than VCM-s, categorised under lower energy consumption.

A comprehensive assessment of these findings highlights the leading position of VCM-vac in terms of energy density, cyclic stability, and energy efficiency. Despite exhibiting a lower kinetic rate, adjusting parameters such as the mass flow rate of humid air, relative humidity, or temperature can mitigate this impact. This indicates that the vacuum impregnation method is more suitable for synthesising thermochemical composite materials compared to other methods.

Fig. 11. Water uptake results for five VCMs across 20 cycles.

#### Table 3

Comparative summary of various performance characteristics of five VCMs.

	VCM- s	VCM-m	VCM- vac	VCM-hp	VCM-htc
Salt on composite surface	Minor	Noticeable	Medium	Medium	Noticeable
Hydration level after hydration (mol/mol)	8.13	4.56	4.00	6.17	5.08
Hydration level after dehydration (mol/mol)	0	0.34	0.48	0.07	0.37
VESD based on particle (GJ/m <sup>3</sup> )	0.83	1.87	2.05	1.05	1.42
Cyclability	Stable	Unstable	Stable	Unstable	Medium
Energy consumption of fabrication (kWh/kg <sub>salt</sub> )	2.93	27.77	3.51	3.78	5.22

Note: Hydration condition: 20 °C, 50 %RH for 12 h; Dehydration conditions: 150 °C for 3 h.

#### 4. Conclusions

This study explores different immersion methods based on the traditional dry impregnation technique to assess their impact on the properties of vermiculite-CaCl<sub>2</sub> composite materials (VCMs). Diverse techniques were employed to analyse structural performance, salt loading, hydration and dehydration characteristics, cycling stability, and energy consumption of fabrication.

Compared to conventional single impregnation, methods like multiple-step immersion, vacuum impregnation, high-pressure impregnation, and high-temperature high-concentration impregnation led to reduced porosity in the synthesised VCMs. Vacuum impregnation significantly aided the infiltration of salt into the pores of vermiculite. VCM-vac showcased a reduction in porosity of almost 30 % compared to RV and nearly 20 % in contrast to control group VCM-s. This reduction is attributed to increased CaCl<sub>2</sub> entry, indicating higher salt content in VCMs synthesised using these methods compared to VCM-s from traditional single impregnation. CaCl<sub>2</sub> content test results support this observation. While VCM-m and VCM-htc show higher porosity than VCM-vac, they accumulate more surface salt, resulting in higher CaCl<sub>2</sub> content than VCM-vac. VCM-m synthesised via multiple-step impregnation exhibits notably elevated salt content at 81.37 wt%, surpassing the highest values reported for vermiculite-CaCl<sub>2</sub> synthesised via single impregnation in previous studies (68 wt%) and the control group (51 wt %) in this study.

During the hydration/dehydration experiments, the five types of VCMs exhibited similar characteristics in their hydration/dehydration reaction rates. In the same environmental conditions (temperature and relative humidity), hydration and dehydration rates were primarily determined by the porosity of the VCMs, with those having higher porosity demonstrating faster hydration and dehydration rates. Among these VCMs, VCM-s and VCM-vac displayed the fastest and slowest reaction rates, respectively. Additionally, the hydration/dehydration rates of these VCMs were also significantly influenced by the relative humidity and temperature of the surrounding gas, with higher relative humidity and temperature facilitating CaCl<sub>2</sub> in the VCMs to faster hydrate.

VCM-vac exhibits the highest volumetric energy density (based on particle) at 2.05 GJ/m<sup>3</sup>. This value is approximately three times the reported literature values and 1.5 times greater than the study's control group VCM-s. It also exceeds the CaCl<sub>2</sub>-rich VCM-m by 0.2 GJ/m<sup>3</sup>. Additionally, VCM-vac exhibits optimal cycling stability due to most CaCl<sub>2</sub> being within its interior, preventing particle agglomeration and reducing CaCl<sub>2</sub> loss in pores. Notably, VCM-s consumes 2.93 kWh/kg during synthesis, with other methods consuming more due to added

processing steps. However, VCM-vac's energy consumption is only around 0.55 kWh/kg higher than VCM-s, indicating relatively lower energy use.

In summary, findings underscore vacuum impregnation as more suitable for synthesising thermochemical composite materials compared to other methods.

#### CRediT authorship contribution statement

**Yong Zhang:** Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Ziwei Chen:** Data curation, Formal analysis, Methodology. **Yanan Zhang:** Investigation, Methodology, Writing – original draft. **Yuehong Su:** Conceptualization, Resources, Supervision, Writing – review & editing. **Saffa Riffat:** Resources, Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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