



A study on vermiculite-based salt mixture composite materials for low-grade thermochemical adsorption heat storage

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ABSTRACT

High-performance renewable energy technologies are desired to meet the enormous demand during the clean energy transition. Thermal energy storage can help balance the mismatch between renewable energy supplies and end-user's demands. Thermochemical adsorption heat storage (TAHS) has attracted widespread attention for its ability to efficiently utilise low-grade renewables and waste heat. Composite adsorbent materials have been gaining increased research interest, which combine hygroscopic salts and host matrix via impregnating salts in the matrix. This paper reviews recent progress in composite materials for TAHS and provides material characterisation analysis on different vermiculite-based composites. The composites use vermiculite as the host matrix with impregnation of different binary and ternary salt mixtures (i.e., $\text{MgSO}_4\text{-CaCl}_2$, $\text{MgCl}_2\text{-LiNO}_3$, $\text{MgSO}_4\text{-LiCl}$ and $\text{MgSO}_4\text{-LiNO}_3\text{-MgCl}_2$). Vermiculite impregnated with a binary mixture of $\text{MgSO}_4\text{-CaCl}_2$ demonstrated a high energy storage density of 1213 kJ/kg, with fast desorption kinetics in the temperature range of low-grade heat. It shows good suitability for domestic TAHS applications, particularly for space heating, with stable cyclic performance over 20 charging-discharging cycles, maintaining approximately 91.3% of its initial energy storage density. The findings of this study contribute to the growing body of research on composite materials and demonstrate the potential of vermiculite-based composites impregnated with binary salt mixtures for low-grade TAHS.

1. Introduction

In recent years, a global decarbonisation transformation has been undergoing in the power sector, with a rapid rise in the share of renewables. Owing to surging fuel prices and demand for cost reduction and low lifecycle emissions, solar and wind technologies have become more competitive and attractive. For instance, renewables generation accounted for 38% of Europe's electricity in 2020, which overtook conventional fossil-fired generation for the first time [1]. More supportive policies have been issued to promote the deployment of renewables for high renewable energy penetration. In 2021, the European Commission lifted the renewables share target to 40% by 2030. Renewable energy-based power generation technologies help domestic and commercial consumers to reduce energy consumption. However, there exists a main gap between the sustainable energy supply and the

energy demand of end-users [2]. Energy storage systems can address the gap by effectively storing the excess energy, which could overcome the temporal or regional difference between the energy supply and demand [3]. This difference could be caused by sudden changes in the energy demand (e.g., peak, and seasonal changes), primary energy and energy conversion devices.

Thermal energy storage (TES) is a technology that stores thermal energy by heating or cooling a thermal storage medium to store energy for later usage in heating, cooling, and power generation applications [4]. TES has been widely employed worldwide with great flexibility across a variety of energy demand sectors, resulting in reductions in greenhouse gas emissions and energy consumption by end-consumers. It is projected by IRENA [5] that the global market for TES could triple in size by 2030. TES applications enable the development of more efficient and integrated energy systems with improved energy performance, thermal reliability, and grid resilience. In particular, a low-grade TES

Abbreviations: DRH, Deliquescence Relative Humidity; DSC, Differential Scanning Calorimetry; ESD, Energy Storage Density; GOA, Graphene Oxide Aerogel; MAX, Maximum; MOF, Metal-Organic Framework; TAHS, Thermochemical Adsorption Heat Storage; TES, Thermal Energy Storage; TGA, Thermogravimetric Analysis; SEM, Scanning Electron Microscope; SG-, Silica gel-based; V-, Vermiculite-based; Z-, Zeolite-based.

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Nomenclature

Symbols

C_{pa}	Specific heat of air (J/(kg•K))
\dot{m}_a	Mass flow rate (kg/s)
Δm_s	Mass change (g)
\dot{P}	Heat release (W)
Q_{release}	Total released heat (kJ)
T_{in}	Air temperature at the reactor inlet (°C)
T_{out}	Air temperature at the reactor outlet (°C)
ΔT	Temperature lift (°C)
U_x	Measured variable relative uncertainty
U_y	Calculated variable relative uncertainty
V_s	Volume (m ³)

system requires an operating temperature below 120 °C, allowing the efficient utilisation of clean energy resources and unrecovered low-grade waste heat that otherwise would have been partially or entirely wasted, for instance, solar energy and various types of waste heat [6]. The low-grade TES systems could be a viable low-carbon solution, contributing to the decarbonisation of heating and cooling in the building sector, energy security and therefore achieving the net-zero target [7].

Depending on the storage medium, there are three main categories of TES technologies, namely, sensible heat storage (e.g., water, sand or rock), latent heat storage (e.g., phase change materials), and thermochemical heat storage (THS) [8]. Both sensible and latent heat storage technologies have been widely applied in different sectors. However, some drawbacks may limit their applications in buildings and industrial processes, for instance, low and short-term energy storage capability with massive volume requirements and notable heat losses [9–11]. THS technology demonstrates high heat storage density, long-term preservation capability, minor heat losses, and good temperature upgrading ability [12,13]. Depending on the working pair in the THS system, THS systems could have a physisorption process with an adsorbent material, an absorption process with a hygroscopic solution or a salt hydrate [14]. Specifically, thermochemical adsorption heat storage (TAHS) is based on the reversible sorption process between the solid adsorbent and the adsorbate vapour, with which heat is stored through the endothermic desorption process and is released through the exothermic adsorption process. There are different types of chemical sorption reactions for TAHS systems based on the selected working pair, for instance, a hydrated salt pair with the hydration-dehydration reactions [15].

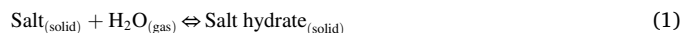
The selection of the thermochemical materials plays a vital role in the TAHS system performance. Substantial research reported on the salt hydrate-based TAHS systems, for instance, using hygroscopic inorganic salts, calcium chloride (CaCl₂), lithium chloride (LiCl), magnesium sulfate (MgSO₄) as the heat storage material with the potential of high heat storage capability and fast reaction kinetics [6,16,17]. In addition to employing pure salt hydrates in TAHS systems, composite adsorbent materials have been gaining increased research interest in recent years, which could address salt deliquescence-related issues. A composite adsorbent material is also called a ‘salt in the porous matrix’, in which a hygroscopic salt is embedded in a host matrix. Typically, the composite material is synthesised through the impregnation of the matrix with an aqueous salt solution [18]. A number of studies have been performed on adopting composite materials in TAHS systems, which could be beneficial for short-term and even seasonal energy storage in domestic and industrial applications. A review of the state-of-the-art composite adsorbent materials suitable for low-grade TAHS systems is presented in this study. Current research mainly focuses on synthesising and evaluating composite materials with the impregnation of a single hygroscopic salt, while limited explorations focus on composites with binary or

ternary salt mixtures for low-grade TAHS systems. Research demonstrates that the impregnation of the salt mixture into a host matrix could lead to achieving a balance between the heat storage capacity and the hydration rate [19]. The present work uses vermiculite as the host matrix to incorporate different salt mixtures. Vermiculite has a high surface area, allowing for large salt loading with chemical stability. There is currently a lack of characterisation data on various vermiculite-based composite materials for low-grade TAHS applications, especially those impregnated with binary or ternary salt mixtures. Therefore, we attempted to synthesise and characterise vermiculite-based salt mixture composite materials. The compositions of the salt mixture include CaCl₂ with MgSO₄; magnesium chloride (MgCl₂) with lithium nitrate (LiNO₃); MgSO₄ with LiCl; and MgSO₄, LiNO₃ with MgCl₂. Furthermore, the characterisation analysis and cyclability assessment of the vermiculite-based composites provide the understanding of the material properties and potential applicability for low-grade TAHS. New insight is provided by expanding the application of vermiculite-based salt mixture composite materials in the field of reliable low-grade thermochemical storage materials for space heating, which can guide further research and development in this area and ultimately help accelerate the clean energy transition.

2. Composite materials for low-grade TAHS systems

For heat storage, the reaction of a hygroscopic salt with water vapour is exothermic as the hydration energy exceeds their lattice energy with heat released. Salts are deliquescent and will dissolve without proper containment within a host matrix. In particular, the deliquescence relative humidity (DRH) value of a hygroscopic salt determines its sorption ability [20]. Salt deliquescence occurs when the relative humidity of the environment is at or above the DRH of the salt or the mutual DRH of the salt mixture, as expressed in the following equations [21]:

For relative humidity of the environment < DRH:



For relative humidity of the environment \geq DRH:



Therefore, the salts for impregnating in the composite should preferably have high water uptake under high relative humidity levels but not easily deliquescent under ambient conditions. Composite materials address the salt deliquescence issues during the hydration process. By impregnating the salts into a host matrix, a balance between the energy storage capacity and the discharging process rate of the thermochemical material can be achieved.

In this study, the composites with low charging temperatures (e.g., <120 °C) are of interest. Based on the literature review, there are a number of candidates of hygroscopic salts for composite adsorbent materials in low-grade TAHS applications, such as calcium chloride (CaCl₂), magnesium sulfate (MgSO₄), magnesium chloride (MgCl₂), lithium nitrate (LiNO₃), potassium carbonate (K₂CO₃), strontium bromide (SrBr₂), and strontium chloride (SrCl₂).

Their respective properties are summarised in Table 1, including volumetric energy density, DRH at 25 °C, dehydration temperature and cost level. CaCl₂ is one of the most promising sorbents with the advantages of easy availability, low cost, high sorption rate, good chemical stability, low corrosiveness, and non-toxicity. Comparatively, MgSO₄, LiCl, MgCl₂, SrBr₂ and SrCl₂ are the preferred salt hydrates for TAHS systems owing to their high theoretical volumetric energy storage densities (i.e., >2.1 GJ/m³). By adopting high energy-density hydrates, less volume is required for storage, which could be beneficial for domestic TAHS applications. In particular, SrCl₂, which exhibits the highest theoretical energy density of 4.9 GJ/m³, is a relatively new salt used in thermochemical heat storage research. For domestic TAHS applications,

Table 1
Specifications of hygroscopic salts [9,17,22–25].

Salts	Volumetric Energy Density	DRH at 25 °C	Dehydration Temperature	Cost
	GJ/m ³	%	°C	
K ₂ CO ₃	1.3	43	93	Low
CaCl ₂	2.2	28	45	Low
LiNO ₃	1.8	13	93	Moderate
MgCl ₂	2.1	33	>150	Moderate
SrBr ₂	2.2	60	90	High
LiCl	2.4	11	65.6	High
MgSO ₄	2.8	92	>120	Moderate
SrCl ₂	4.9	12	61	Moderate

the low-cost K₂CO₃ has been investigated because its hydration reaction can occur at the ambient temperature and with low dehydration temperature (i.e., 93 °C).

2.1. Host matrix materials

It is noteworthy that the energy storage performance of a synthesised composite material varies depending on the host matrix and the immersed salts, which implies the importance of optimal material selection and composition. Typically, a host matrix has a large pore volume with a mesoporous structure (e.g., an ideal pore size range of 2–50 nm), which can facilitate salt impregnation and benefit the kinetics of moisture migration [26]. Additionally, the structural stability of the host matrix is also an essential factor for consideration to ensure the stable multicyclic performance of a TAHS system [27]. In this section, a review of the available composite materials with charging/desorption temperatures below 120 °C reported in the literature is presented. The targeted host materials include silica gel, zeolite, vermiculite, metal-organic framework, graphene oxide aerogel and pumice.

Silica gel (SG) is the most commonly used host material, with features of chemical inertness, toxic-free, long life, low abrasion, low cost, and great feasibility under different conditions [28,29]. Extensive studies have been conducted on SG-based composites with various hygroscopic salt combinations for low-grade heat storage applications. For instance, Courbon et al. [30] synthesised a composite of SG-CaCl₂ (43 wt %), which demonstrated a high volumetric energy storage density of 211 kWh/m³ (i.e., with adsorption reaction at 30 °C and desorption reaction at 80 °C). Their results reveal that the SG-CaCl₂ composite can be feasible for the TAHS systems by integrating solar thermal collectors. On the other hand, they also assessed the feasibility of an SG-SrBr₂ composite for the solar-assisted TAHS system, which provided a similar volumetric energy storage density of 203 kWh/m³ as the SG-CaCl₂ composite [31]. In order to store the low-grade solar thermal energy for space heating applications, Zhu et al. [32] investigated the kinetic hydration/dehydration behaviour of an SG-SrCl₂ composite, and a volumetric energy storage density of 171 kWh/m³ was achieved. The composite showed good cyclic performance over 30 cycles under the adsorption condition of 20 °C, 60% RH with a desorption temperature of 100 °C. Yu et al. [33] proved the stable heat storage performance of an SG-LiCl (30 wt%) composite with a volumetric energy density of 163.6 kWh/m³ and a desorption temperature of 80 °C. Owing to the low cost, non-corrosiveness and low desorption temperature (i.e., 40–50 °C), Jarimi et al. [19] tested a composite based on silica gel and potassium formate, which displayed an energy storage density of 457 kJ/kg.

Zeolite (Z) presents a regular nanoporous structure. Zeolites have been favourable host matrices with impregnation with different salts. Among various types of zeolites, synthetic zeolite 13X, with the largest permeability and high stability, offers outstanding suitability for thermochemical energy storage applications [34–36]. Whiting et al. [37] characterised two different zeolite-based composites, including Z-MgSO₄ (15 wt%) with an energy density of 970 kJ/kg and Z-MgCl₂ with an energy density of 1173 kJ/kg. The Z-MgCl₂ composite presented

better heat storage performance, owing to the higher storage density of MgCl₂ and the blocking issue in the host matrix caused by the MgSO₄ particles. Researchers also found that one of the main challenges for zeolitic composites is their comparatively high dehydration temperatures (i.e., >120 °C) for integration with low-grade heat sources and high costs [38]. To address the issues, Rehman et al. [39] prepared a novel zeolite-based composite with a binary salt mixture of MgSO₄ (90%) and ZnSO₄ (i.e., Zinc Sulfate, 10%), which had an energy storage density of 1422 kJ/kg. Their powder X-ray diffraction analysis showed the dehydration reaction temperature of the composite is 120 °C.

Vermiculite (V) is a natural and non-toxic mineral. Structurally, vermiculite is a mixed-layered silicate crystal. The environmentally-friendly vermiculite has been widely used as an active carrier for adsorbents, filter aids, chemicals, and fertilisers. As the host matrix, the lightweight vermiculite allows the reaction process to be more easily controlled and supplies energy when necessary [40–42]. For instance, Casey et al. [43] examined the V-CaCl₂ composite with a volumetric energy storage density of 290 kWh/m³ and a charging temperature of 90 °C, which could be suitable for domestic thermal energy storage applications. The characterisation analysis carried out by Jarimi et al. [19] suggested that the vermiculite-based composites are appealing for long-term energy storage in building applications, owing to the features of flexibility, availability, low cost and low charging temperature below 80 °C. Brancato et al. [26] observed a slower reaction kinetic in the vermiculite-based composites (i.e., impregnated with LiCl and LiBr, respectively) compared with the SG-based composites. They reported that the V-LiCl composite has a volumetric energy density of 111 kWh/m³ and a desorption temperature of 90 °C. Zhang et al. [44] measured the energy storage performance of a V-SrBr₂ composite, with an energy storage density of 0.46 kWh/kg and a volumetric energy storage density of 105.36 kWh/m³. Moreover, Shkatulov et al. [45] investigated the chemical, textural and performance stability of the V-K₂CO₃ (63 wt%) composite, and a volumetric energy storage density of 250 kWh/m³ was obtained. They also conducted a cyclic performance study and confirmed that the V-K₂CO₃ composite could stably perform for over 47 cycles of charging and discharging.

Metal-organic framework (MOF) represents an emerging class of crystalline hybrid porous materials obtained by assembling metal nodes and organic ligands [46]. MOFs have been explored with good hydrothermal stability, water adsorption isotherms and low charging temperatures (90–140 °C) [47]. MOFs have been widely accepted in industrial applications, such as gas and electronics applications. However, there are limited studies on the MOF-based composites in TAHS applications, which require further research and development. For instance, the MIL-100(Fe)-CaCl₂ (46 wt%) and MIL-101(Cr)-CaCl₂ (62 wt%) composites have been reported with high volumetric energy storage densities of 208 kWh/m³ and 310 kWh/m³, respectively and low desorption temperature of 80 °C [48]. Minor losses have been noticed upon multiple adsorption-desorption cycling tests, and the two composites also offered high chemical stability based on the 18-month ageing observation. D'Ans et al. [49] prepared and characterised a novel composite of MIL-101(Cr)-SrBr₂ (63 wt %) with a volumetric energy storage density of 233 kWh/m³ at a desorption temperature of 80 °C. The composite could be suitable for seasonal solar energy storage and space heating of low-energy buildings.

Graphene oxide aerogel (GOA) has a 3D porous network structure with remarkably high porosity (97%), a large specific surface area, low density, and good thermal conductivity [50,51]. GOA can be a promising candidate as a host matrix, which increases the loading rate of salt hydrates in the composites and improves heat transferring and water vapour transporting throughout salt hydrates. Zhou and Zhang [52] suggested that GOA could be an excellent host matrix and found that the GOA-MgCl₂ (90 wt%) composite has an energy storage density of 1598 kJ/kg but a relatively high regeneration temperature (i.e., >120 °C). Yan et al. [53] developed an ultrahigh-energy/power-density sorption thermal battery based on the GOA-CaCl₂ (96 wt%) composite,

demonstrating an excellent energy density of 7768 kJ/kg with a regeneration temperature of 80 °C. Furthermore, MOF/graphene-derived nanocomposites have been newly developed, which can be considered alternative candidates to provide high specific surface area and improved thermal conductivity with low charging temperature and high sorption capacity [54].

Pumice is a porous pyroclastic rock with a porosity of 64–85% (by volume), which has been widely used in agriculture applications due to its large water-holding capacity to store and slow-release water for plant watering [55]. Pumice, with high structural strength and rigidity, is resistant to compression and bending, which could be a suitable matrix material for combining with different hygroscopic salts [56]. The pumice-based composites are still under research, with a few studies reported in the literature. For instance, Mehrabadi and Farid [56] synthesised a novel pumice-SrCl₂ (14 wt%) composite. Although the composite had a low volumetric energy density of 22 kWh/m³, outstanding mechanical strength and cyclic stability were observed.

Instead of impregnating a single hygroscopic salt, attention has also been paid to salt mixtures with various salt combinations. Salt mixtures can address the shortcomings that a pure hygroscopic salt may have, for example, the multicyclic stability, kinetic behaviour of adsorption-desorption, and high charging temperature. Posern and Kaps [21] proposed an attapulgite-based composite material using a combination of MgCl₂ and MgSO₄. By partially substituting MgSO₄ by MgCl₂, the deliquescence relative humidity of the mixture was reduced. They measured the energy density of the composite heat storage material containing a salt mixture of 20 wt% MgSO₄, and 80 wt% MgCl₂ was 1590 kJ/kg by calorimetry. The study conducted by Rammelberg et al. [57] demonstrated that combining CaCl₂ with MgCl₂ of relatively steadier hygrothermal performance led to improvements in the cyclability, mass and enthalpy balance. Zhao et al. [58] synthesised a composite adsorbent by impregnating zeolite 13× with a binary salt mixture of LiCl and CaCl₂, leading to a significant enhancement in the adsorption capacity. Chen et al. [59] used 3A zeolite as the host matrix, impregnated it with a binary salt mixture of LiCl and LiBr and found a noticeable increase in the heat storage density to 585.3 kJ/kg, which was 30.9% higher than that of pure zeolite. However, a few studies have investigated vermiculite-based composite materials with binary or ternary salt mixtures, and further research and development are still needed to advance low-grade TAHS systems.

3. Synthesis and characterisation of vermiculite-based salt mixture composite materials

3.1. Composite material synthesis

In this study, vermiculite-based composite materials are considered for experimental investigation of the feasibility of low-grade TAHS systems. As the host matrix, vermiculite is featured with lightweight, high porosity, low charging temperature (e.g., 80 °C), low costs, low mechanical strength, chemically non-reactive, fire-resistant, odourless, and durable. The loose-fill vermiculite was purchased from Fisher Scientific UK Ltd with a controlled particle size distribution. The thermophysical properties of vermiculite are listed in Table 2. The macropores structure of vermiculite can facilitate salt impregnation and benefit the kinetics of moisture adsorption [60].

Different vermiculite-based composites were synthesised with different binary salt mixtures impregnated for improved sorption kinetics and hygrothermal performance, including V–CaCl₂–MgSO₄, V–MgCl₂–LiNO₃, and V–MgSO₄–LiCl, and a ternary salt mixture

Table 2
Thermophysical properties of vermiculite [2,41,61].

	Specific Heat	Specific Surface Area	Porosity
Vermiculite	1.08 kJ/kg·K	8–15 m ² /g	2.84 cm ³ /g

V–MgSO₄–LiNO₃–MgCl₂. All salts were purchased from Merck Life Science UK Ltd in anhydrous state. As mentioned in Table 1, MgSO₄ exhibits a relatively high energy density (2.8 GJ/m³). Researchers have pointed out that its main disadvantage is the slow sorption kinetics. Xu et al. [62] suggested that MgSO₄ is suitable for impregnation in composite materials in low-temperature TAHS applications, which could alleviate the kinetic issue in the hydration reaction. In this study, we proposed the combinations of MgSO₄ with salts of fast sorption kinetics, for example, CaCl₂ and LiCl. On the other hand, CaCl₂ has a relatively low DRH (i.e., 28% at 25 °C), resulting in an unsteady thermal performance during the reaction process. Combining with MgSO₄, which has a higher DRH, could enhance the hygrothermal performance. The salt mixture of CaCl₂–MgSO₄ has been investigated with good cyclability and kinetic sorption properties [57]. Although MgCl₂ is featured with fast sorption kinetics and high energy storage density, its dehydration temperature is high (i.e., >150 °C). Therefore, we proposed the salt mixture of MgCl₂–LiNO₃, combining MgCl₂ with LiNO₃ of a lower dehydration temperature (i.e., 93 °C). However, both MgCl₂ and LiNO₃ have relatively low DRH values at the given temperature level (i.e., 33% and 12%, respectively, at 25 °C), hence a ternary salt mixture of MgSO₄–LiNO₃–MgCl₂ was considered to tackle the possible deliquescence issue, by combining MgSO₄ with a high DRH value (i.e., 92% at 25 °C).

For the binary salt mixtures, the mass mixing ratios of the saturated solutions are 2:1 for CaCl₂–MgSO₄, 1:1 for MgCl₂–LiNO₃, and 1:1 for MgSO₄–LiCl. For the ternary salt mixture, the mass mixing ratio is 1:1:1 for MgSO₄–LiNO₃–MgCl₂. These mass mixing ratios and the amount of required saturated salt solutions were determined based on the preliminary study that evaluated the adsorption capacity of the vermiculite by analysing its porosity. To reduce the charging/dehydration temperature of the composite, a mass mixing ratio of 2:1 was selected for the CaCl₂–MgSO₄ mixture, with a higher proportion of CaCl₂ due to its lower dehydration temperature.

To synthesise a vermiculite-based composite, five steps were followed based on the method pioneered by Aristov et al. [63]. Fig. 1 shows the synthesis procedure and photos of the steps of the V–CaCl₂–MgSO₄ composite.

1. Weighed the required amount of vermiculite (i.e., 600 g) and thoroughly dried it using an oven at 200 °C for complete removal of water;
2. Prepared the mixed saturated salt solution (i.e., 1800 g) using a magnetic stirrer and left the mixed salt solution at room temperature;
3. Once the temperature of the saturated salt mixture solution was the same as room temperature, mixed the solution with the dried vermiculite by adding the solution into the vermiculite in a container and constantly stirring as the salt solution soaked into the pores of vermiculite;
4. Let the synthesised vermiculite composite for at least 24 h to ensure the vermiculite was uniformly impregnated by the salts by observing whether a thoroughly wetted transition takes place;
5. Dried the wetted composite material by placing it into an oven at 200 °C to evaporate the water for complete dehydration and ensure the salts are confined within the vermiculite (e.g., the dried V–CaCl₂–MgSO₄ composite had a final weight of 1342 g and density of 42.37 kg/m³).

3.2. Scanning Electron Microscope analysis

Scanning Electron Microscope (SEM) was used to visualise the morphology and microstructure of the synthesised vermiculite-based composites. It can also be used to observe whether the hygroscopic salt mixture is binding uniformly inside the matrix of vermiculite for improved mass and heat transfer performance. An energy dispersive X-ray microanalysis (EDX) system was adopted, which is JEOL JSM-6060LV. The samples were completely dried in an oven to remove

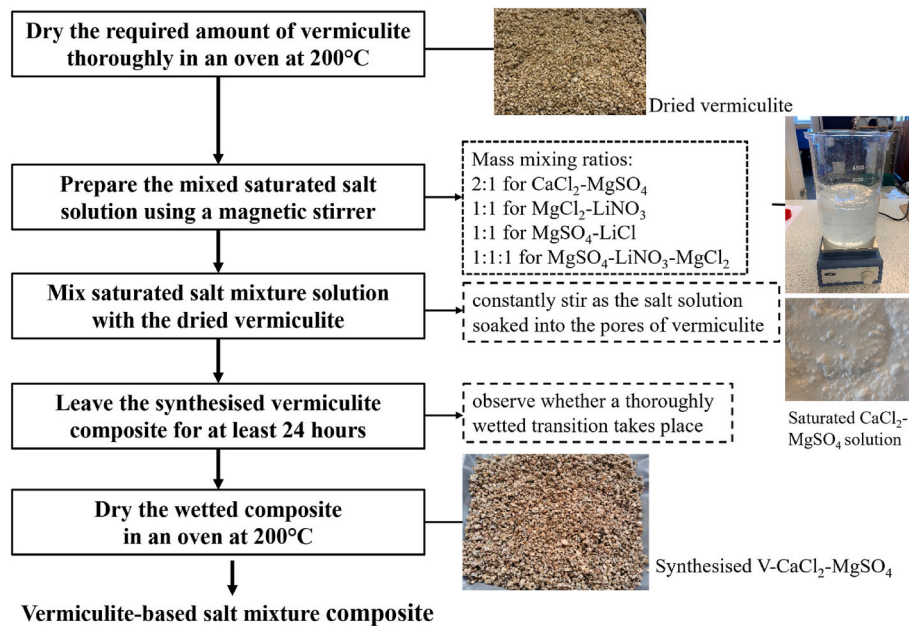


Fig. 1. Fabrication procedure of vermiculite-based salt mixture composite materials.

inhaled moisture, which could affect the characterisation results. Fig. 2 presents the SEM photos of pure vermiculite and three different vermiculite-based composites. As seen, the raw vermiculite with a layered porous structure has thin lamellas that provide sufficient surface area for accommodating a significant quantity of salts. The SEM fracture photos of the vermiculite-based composites confirm that the impregnation of the salt mixture leads to a visible change in the vermiculite morphology. Salts are evenly embedded in the entire vermiculite surface and its pore surfaces. Unlike the smooth surface texture of raw

vermiculite, the vermiculite composites have noticeable fragments on lamellas, which may be caused by the swelling effect and possible intercalation between silicate layers with the treatment of salt mixture.

3.3. Material characterisation analysis

In this study, the experiments were performed with a Thermal Analyzer Instrument SDT-Q600, which can deliver simultaneous measurement of weight change (i.e., Thermogravimetric Analysis, TGA) and

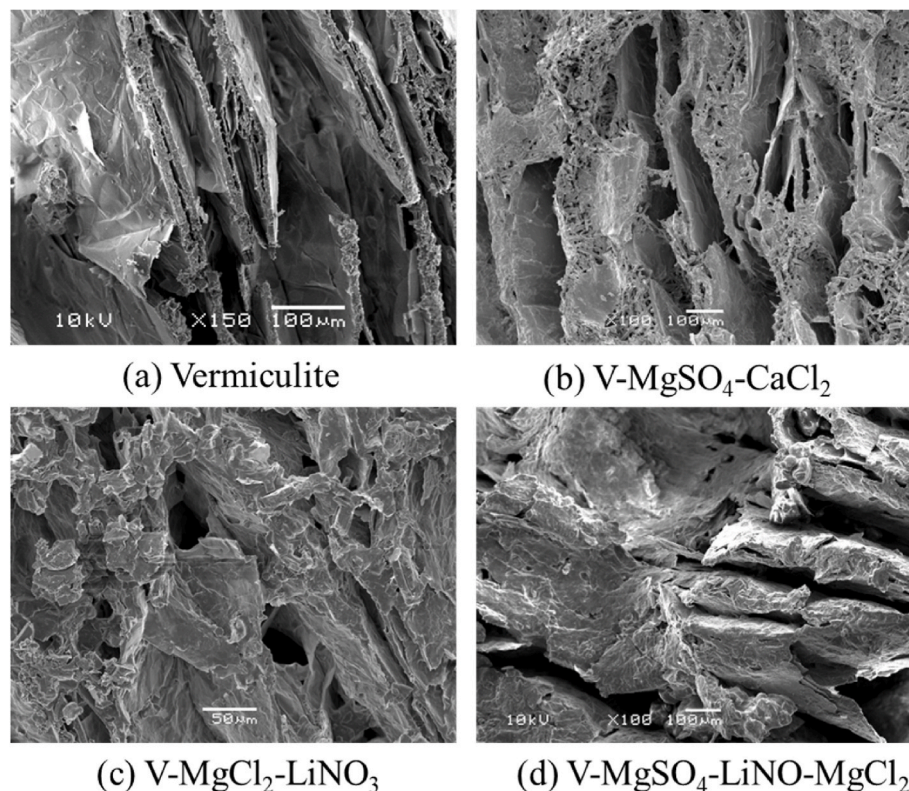


Fig. 2. SEM photos of raw vermiculite and vermiculite-based salt mixture composite materials.

heat flow (i.e., Differential Scanning Calorimetry, DSC) on the sample material in the range of ambient temperature to 1500 °C under air or nitrogen flow. For testing, wet samples of the vermiculite-based composites were prepared, ensuring the specific moisture content of the sample materials reached 95 %RH. Prior to testing each sample, a baseline measurement was conducted using two empty alumina pans in the temperature range of ambient temperature to 150 °C at a constant rate of 5 °C/min in an inert nitrogen atmosphere and cooling with the ambient air whilst the weight of the cups was continuously measured along with the heat flow. Subsequently, the sample (i.e., with a weight of 35 mg) was placed in one of the cups, and the measuring process was carried out. The average integral reading (J/g) in the temperature range of 20–150 °C was taken. Multiple samples of the composite materials are required in order to obtain the energy density result with minimised sampling uncertainty. In this study, each synthesised vermiculite-based composite was prepared in triplicate, with each sample having the same weight. Repeated energy density tests were performed for every composite to ensure reproducibility and avoid faulty samples or invalid measurements.

Fig. 3 presents the TGA results of the four vermiculite-based composites. Upon exposure to the testing condition, the wet samples initiated water release but displayed varying desorption behaviours. Comparatively, V-CaCl₂-MgSO₄ demonstrates fast kinetics of water release, with the highest mass loss (i.e., 58.25%) in the temperature range of 20–150 °C. For instance, within the temperature range of 20–60 °C, V-CaCl₂-MgSO₄ has a high rate of water loss, while the other three composites have a similar tendency to dehydrate much slower. At 60 °C, V-CaCl₂-MgSO₄ has approximately 14% weight loss, whereas V-MgCl₂-LiNO₃ has 9% and only around 7% for V-MgSO₄-LiCl and V-MgSO₄-LiNO₃-MgCl₂. At 80 °C, the weight loss is 30% for V-CaCl₂-MgSO₄, 20% for V-MgCl₂-LiNO₃ and approximately 15% for V-MgSO₄-LiCl and V-MgSO₄-LiNO₃-MgCl₂.

The fast desorption kinetics of V-CaCl₂-MgSO₄ may be attributed to the unique salt mixture of CaCl₂ and MgSO₄. The high water adsorption capabilities of these salts facilitate the rapid release of water during the dehydration process. Since the salt mixtures differ for each composite, the strength of the interactions between the water molecules and the composite and the ease with which the water molecules can be released are different. By impregnating the salt mixture of CaCl₂ and MgSO₄, the resultant composite has weaker reformed chemical bonds between salt and water molecules, making it easier for the composite to release water molecules during the dehydration process.

Fig. 4 provides the graphs of heat flow against temperature obtained from the DSC measurements. With the data analysis software (i.e.,

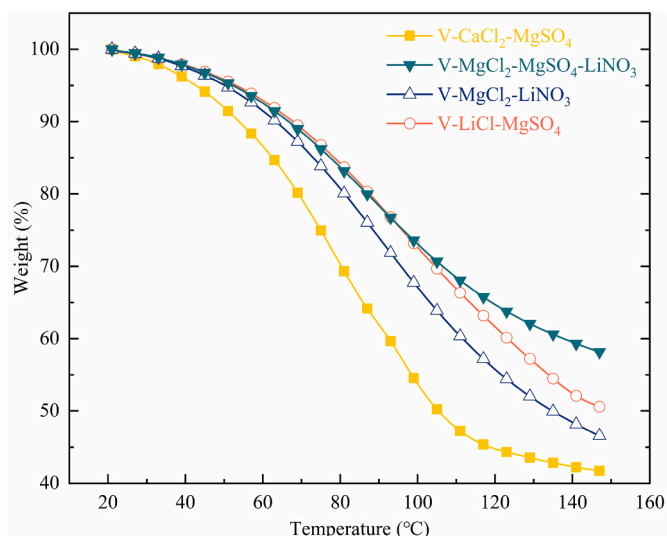


Fig. 3. TGA results of vermiculite-based salt mixture composite materials.

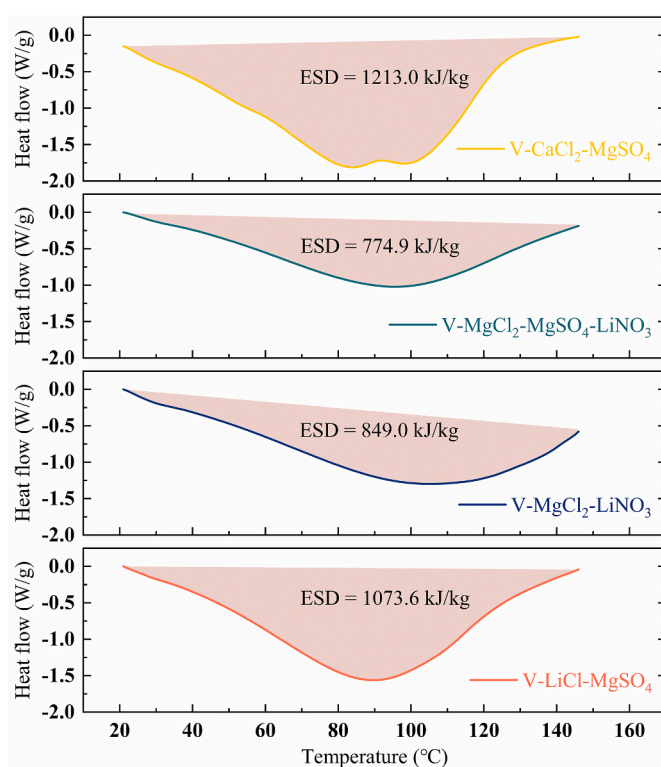


Fig. 4. DSC results of vermiculite-based salt mixture composite materials.

Universal Analysis Software 2000), the obtained DSC result was subtracted from the corresponding baseline result, and the energy storage density (ESD) of the composite was derived by performing the embedded Running Integral analysis function. The energy density of the vermiculite-based composite was determined based on the average result of the three tests. Among all composites, the reformation and recombination of the two salts, MgSO₄ and CaCl₂, contributed to the highest energy density, 1213 kJ/kg. Comparatively, the impregnation of the ternary salt mixture (i.e., MgSO₄-LiNO₃-MgCl₂) did not lead to an increase in the overall energy density (i.e., 774.9 kJ/kg). It is perhaps because the recreated crystalline salts on the vermiculite surface affected the sorption kinetics of the synthesised composite.

3.4. Moisture vapour adsorption isotherm characterisation

Moisture vapour adsorption isotherms of the four composite materials were obtained using dynamic vapour sorption in accordance with the BS EN ISO 12571:2013 guidelines. The experiment was conducted in a laboratory incubator with precise temperature control (Fig. 5). The moisture uptake performances of the composites were analysed at the relative humidity level of 45 %RH and a constant temperature of 25 °C. A magnesium chloride saturated solution was employed inside the chamber to achieve the internal relative humidity level. Prior to testing, the desired internal relative humidity level was maintained for a period to ensure accuracy. All samples were dried in the oven at 150 °C for 24 h to attain complete dryness and then cooled down in a vacuum seal container until to room temperature before testing. Weight variations of the composite were quantified using a micro load cell with a capacity range of 0–100 g, connected to a data logger for signal amplification and electrical output measurement. Each test was conducted for 20 h.

Fig. 6 presents the water uptake performances of the four composites at a humidity level of 45 %RH. The composites displayed varying moisture sorption kinetics due to the differences in salt mixtures. The results show that the V-CaCl₂-MgSO₄ composite has a high affinity for water molecules, with the highest water uptake ratio of 0.42 g/g after

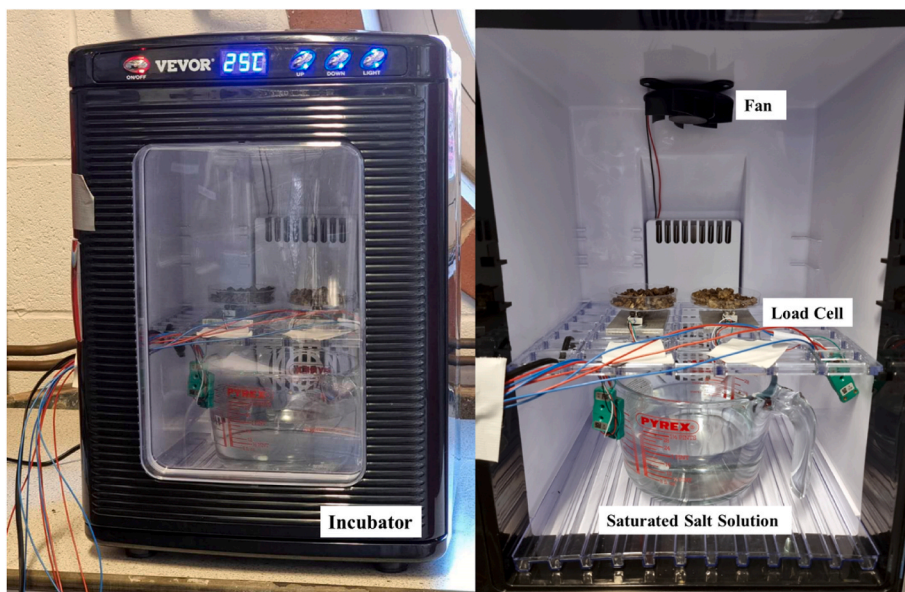


Fig. 5. Photos of the incubator with an internal view.

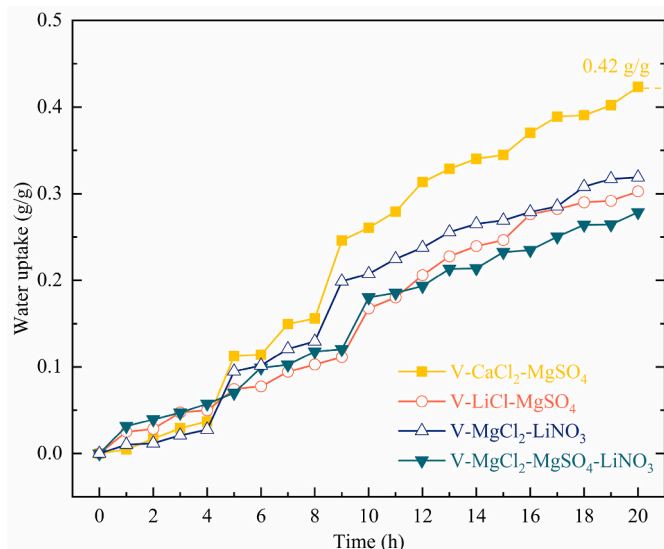


Fig. 6. Water uptake variations of four composites.

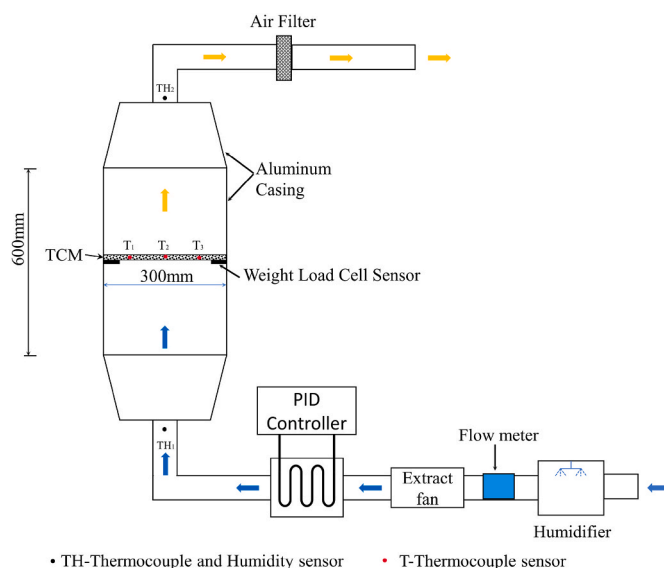
20 h, followed by V-MgCl₂-LiNO₃ with a ratio of 0.32 g/g. The water uptake ratios among V-MgSO₄-LiCl, V-MgCl₂-LiNO₃ and V-MgSO₄-LiNO₃-MgCl₂ are similar, with a slight difference after the 20 h of sorption testing. Notably, V-MgSO₄-LiNO₃-MgCl₂ with the ternary salt mixture has the lowest water uptake ratio of 0.28 g/g. V-CaCl₂-MgSO₄ had a slower initial water uptake ratio between 0 and 4 h. This could be because of the presence of vermiculite with a layered structure that can impede the movement of water molecules. The progressive formation of hydrated calcium chloride and magnesium sulfate within the composite leads to significant increases in water uptake ratio at the 4th and 8th hour, respectively.

4. Cyclability testing

Because of its high energy density, fast dehydration kinetic and excellent water uptake performance, the V-CaCl₂-MgSO₄ composite was chosen to further assess its feasibility and cyclic stability for heat storage in domestic applications, e.g., space heating. It is important to

first establish the feasibility and cyclic stability of the composite material under controlled laboratory conditions before scaling up to real-world conditions. The composite is intended to operate within a temperature range of approximately 20–120 °C and at atmospheric pressure during the charging and discharging processes. Therefore, a versatile lab-scale test rig was constructed for experimental analysis. The test rig is designed to ensure efficient air flow through the packed composite material particles, and its schematic diagram is presented in Fig. 7. The test rig is composed of multiple components, with the primary unit being a reaction chamber that houses the V-CaCl₂-MgSO₄ composite particles within a mesh drawer. A humidifier provides moist air during the discharging process, while a fan circulates air within the chamber. To facilitate charging process, an electric heater is located downstream of the fan and serves as the primary heat source. A PID controller is implemented to regulate the heating temperature. All components are interconnected under standard atmospheric pressure, with air circulating within the chamber linked to the ambient environment.

As seen in Fig. 8, the V-CaCl₂-MgSO₄ composites are held within a



• TH-Thermocouple and Humidity sensor • T-Thermocouple sensor

Fig. 7. Schematic diagram of the thermochemical reaction chamber.

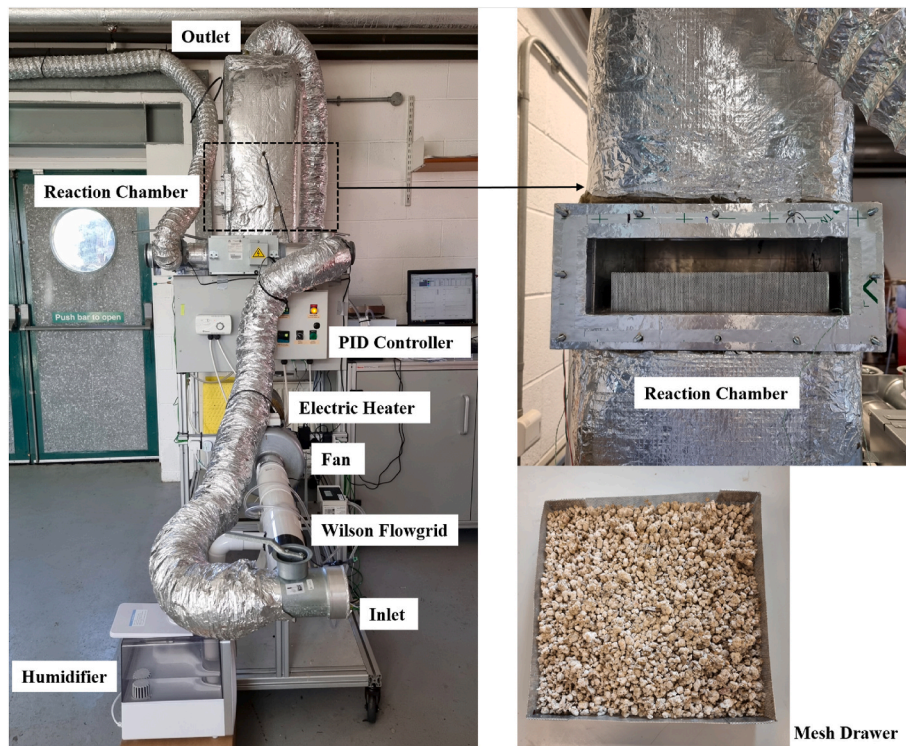


Fig. 8. Photos of the test rig and internal view of the reaction chamber.

mesh drawer that can be easily removed and re-inserted into the reaction chamber. The drawer is designed for convenience, enabling easy access to the material for inspection or replacement. The open nature of the mesh design provides a large surface area for air to interact with the composite materials, allowing for effective heat and mass transfer.

Table 3 lists the measurement instrument with their specifications. A Wilson Flowgrid was installed for in-duct air velocity measurement. Both temperature and humidity sensors were placed at the inlet and outlet of the reaction chamber to monitor and record the corresponding relative humidity level of the airflow. In addition, temperature sensors were installed at different locations, such as at the inlet, outlet inside the reaction chamber, and mesh drawer. The data were collected every second.

Temperature sensors used in the experiment were calibrated before use to ensure accurate temperature measurements. The calibration process involved comparing sensor readings against a reference temperature (i.e., using an ice bath and boiling water at standard atmospheric pressure) and making adjustments to minimise systematic errors. An uncertainty analysis is also considered to determine the level of error associated with calculated values for evaluation parameters. To achieve this, a function that links the measured physical parameters to the calculated parameter is employed, as detailed in Refs. [64,65]:

$$U_y = \sqrt{\sum_{i=1}^N U_{x_i}^2} \quad (3)$$

Where U_y and U_{x_i} are relative uncertainties of the calculated parameter y

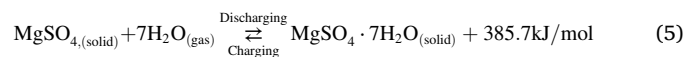
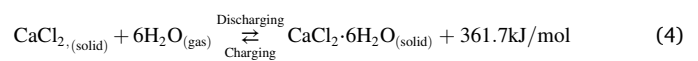
Table 3
Specifications of measurement instruments.

Devices	Measurement Range	Accuracy
Sensirion humidity sensor	-40-125 °C	±0.3%
	0-100% RH	±2%
K-type thermocouple	0-1100 °C	±0.75%
Wilson Flowgrid	0-60 m/s	±1%
DataTaker DT80	-	±0.1%

and each measured variable x_i . In this study, the total uncertainty is about ±2.3% according to the accuracies of the instruments, as listed in Table 3.

The experimental work was conducted in a temperature-controlled laboratory. The operating inlet air condition for the discharging process was maintained in the temperature range of 17–19 °C and relative humidity of 70–80 %RH with a constant airflow mass flow rate of 0.023 kg/s. In the testing, the performance of the thermochemical reaction chamber is mainly evaluated by the temperature lift factor (i.e., ΔT), which is determined by the temperature difference between the inlet and outlet of the reaction chamber. For this assessment, the discharging process was considered complete when $\Delta T \leq 5$ °C, and the charging process was considered complete when $\Delta T \cong 0$ °C.

The reaction process can be expressed as follows:



In total, 20 cycles of charging and discharging were implemented. Fig. 9 displays variations of the temperature lift ΔT during the 1st, 5th, 10th, 15th, and 20th discharging processes. These particular cycles were selected to represent the range of results throughout the testing process. Upon initiating the discharging process, the V–CaCl₂–MgSO₄ composite exhibited an immediate heat release, resulting in a rapid increase in temperature. During the first discharging process, the maximum temperature lift (ΔT_{MAX}) was approximately 13.81 °C. Subsequently, ΔT_{MAX} gradually decreased over the course of the discharging cycles and reached 12.16 °C during the 20th discharging process. The observed temperature lift difference between the first and 20th discharging processes was approximately 1.65 °C, indicating that the V–CaCl₂–MgSO₄ composite can maintain a consistent temperature lifting performance during repeated charging and discharging cycles. The results reveal that the stored energy of the V–CaCl₂–MgSO₄ composite could be utilised for building space heating applications, particularly for low-energy

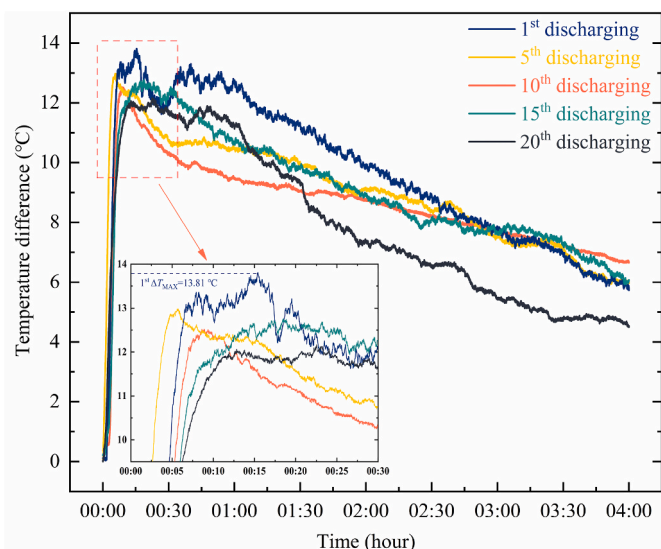


Fig. 9. Temperature lift variations for 20 cycling tests.

buildings with renewable energy integration (e.g., solar and wind energy technologies).

Based on the temperature lift results, the heat release during the discharging process can be obtained:

$$\dot{P} = \dot{m}_a C_{pa} (T_{out} - T_{in}) \quad (6)$$

$$Q_{release} = \int \dot{P} dt \quad (7)$$

where \dot{m}_a is the mass flow rate of airflow, kg/s; C_{pa} is the specific heat of air, J/(kg•K); T_{in} and T_{out} are the airflow temperatures at the inlet and outlet of the reaction chamber, °C, respectively.

The energy storage density of the reactor can be derived by:

$$ESD = Q_{release} / V_s \quad (8)$$

Where V_s is the volume of the V-CaCl₂-MgSO₄ composite.

Fig. 10 depicts the obtained results of the maximum temperature lift (ΔT_{MAX}) and the energy storage density (ESD) during the 1st, 5th, 10th, 15th, and 20th discharging processes. As the number of cycling tests increased, the energy storage density of the reactor decreased progressively, from 197.34 kWh/m³ to 161.01 kWh/m³. Nevertheless, it

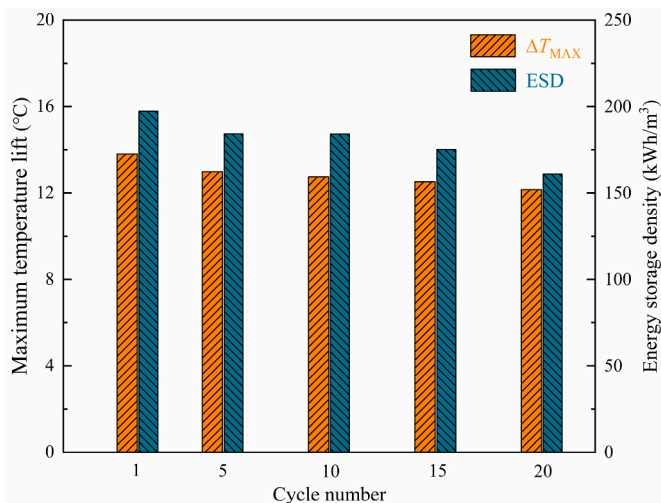


Fig. 10. Results of the maximum temperature lift and energy storage density during 20 cycling tests.

maintained about 82% of its original ESD after 20 cycles, indicating relatively stable cyclic performance.

Fig. 11 presents the SEM photos of the original and cycled composites. After undergoing 20 cycles of charging and discharging, the layered structure of the vermiculite can still be clearly observed. Throughout the cycling process, vermiculite maintains its stability without any visible deterioration in its structural integrity. However, the appearance of the salt changes. Initially, the vermiculite lamellas were coated with irregular-sized salt particles, which also occupied the interlayer spaces. After the cycles, the salt forms clusters of crystallites, which can be noticed in the SEM image at 1000× magnification. The salt particles may crack due to mechanical stress, forming smaller particles, which may re-crystallise during the discharging process, leading to salt dispersion. The SEM analysis confirms the structural stability and durability of the composite for multiple cycling operations.

The DSC-TGA measurement was carried out for the V-CaCl₂-MgSO₄ composite after 20 cycling tests with TA instrument SDT-Q600. The obtained results (as seen in Fig. 12) indicate the composite underwent some degradation over the 20 cycling tests, as a reduction in the dehydration rate of the V-CaCl₂-MgSO₄ composite after cycling tests is observed. During the TGA measurement period, the weight loss of the V-CaCl₂-MgSO₄ composite after cycling tests is 48.72%, while the original composite had a weight loss of 41.59%. This could be attributed to the deliquescence of the salt. Despite undergoing 20 cycles, the V-CaCl₂-MgSO₄ composite still maintained approximately 91.3% of its initial energy storage density. The composite material demonstrated consistent performance over an extended period of use, suggesting its reliability and potential as a viable option for heat storage.

The results confirm the thermal stability of V-CaCl₂-MgSO₄ composite during repeated cycles, which can be attributed to the structural integrity provided by vermiculite, the stabilisation of salt mixture within the matrix, improved kinetics of hydration and dehydration processes, and good compatibility with low-grade heat sources. Shkatulov et al. [45] verified the chemical, morphological and thermal stabilities of V-K₂CO₃ composite. After 74 hydration/dehydration cycles, the composite maintained its structural integrity and exhibited stable conversions over at least 47 cycles with salt deliquescence. Brancato et al. [66] investigated the thermal stability of V-LiCl composite and proved that the composite maintained its sorption ability and physical appearance after 14 consecutive cycles, without significant degradation. These findings highlight the potential of vermiculite-based composites as promising and stable materials for low-grade TAHS systems. Furthermore, Table 4 presents a comparative analysis of the performance of the V-CaCl₂-MgSO₄ composite material synthesised in this study with other salt mixture composite materials reported in the literature, including their energy storage density, and cycling performance. Zeolite has been a favourable host matrix owing to its high thermal stability and structural integrity. Although Z-CaCl₂-MgSO₄ composite exhibited higher ESD than V-CaCl₂-MgSO₄ composite, V-CaCl₂-MgSO₄ demonstrates enhanced thermal stability and cycling performance. These findings reveal the promising potential of this V-CaCl₂-MgSO₄ composite material for low-grade thermochemical heat storage systems.

5. Conclusions

Thermochemical heat storage offers high storage densities, minor heat losses and long-term preservation capability, which can be a promising solution in addressing the mismatch between renewable energy supplies and the end-user's demand. Low-grade thermochemical heat storage systems allow the efficient utilisation of low-grade heat that otherwise would have been partially or entirely wasted. Composite adsorbent materials have attracted increasing interest in the research field of thermochemical adsorption heat storage. Based on the literature review, the available candidates for low-grade TAHS systems include silica gel-based, zeolite-based, vermiculite-based, metal-organic framework-based, graphene oxide aerogel-based and pumice-based

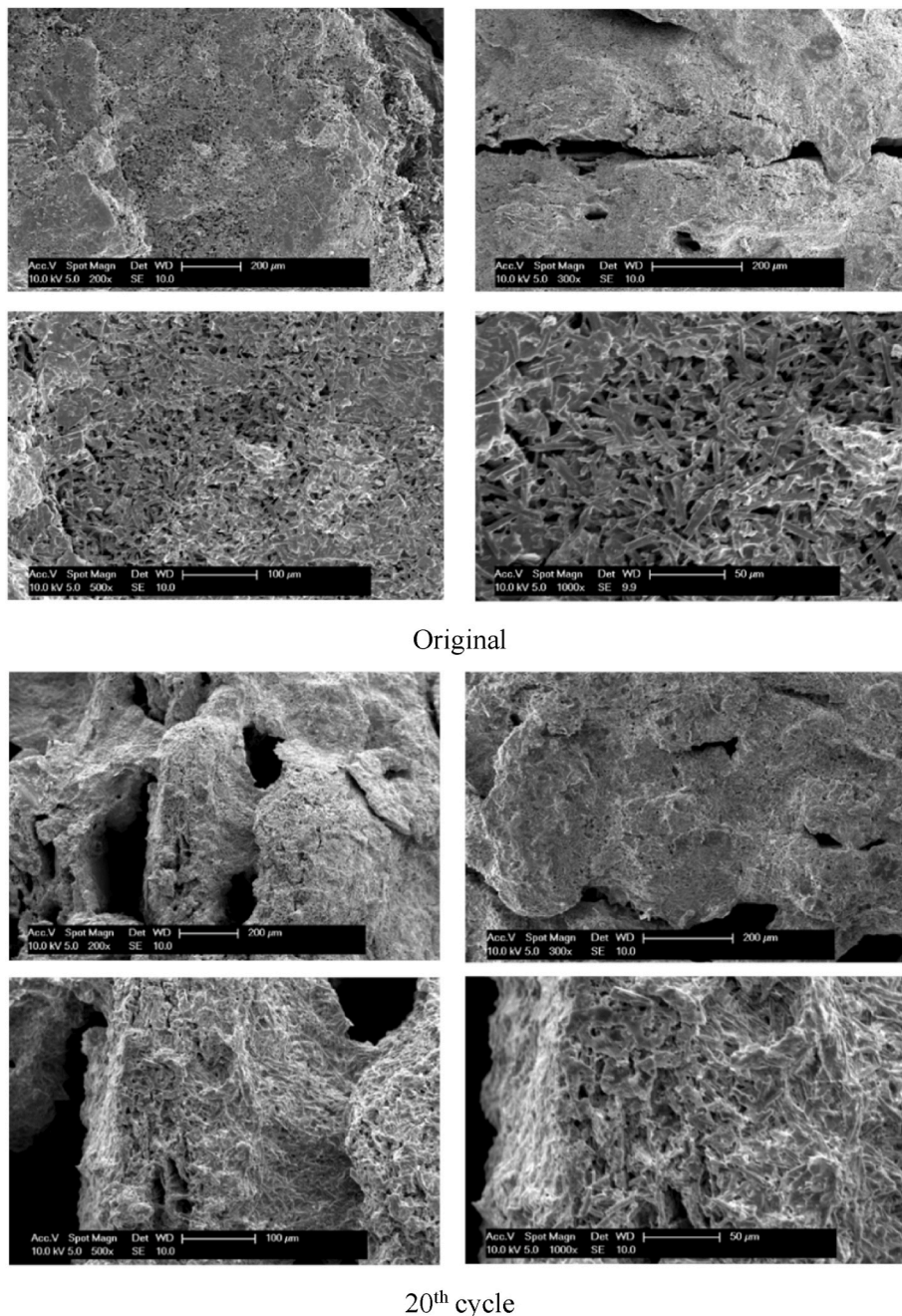


Fig. 11. SEM photos of V-CaCl₂-MgSO₄ composite.

composites.

In this study, four vermiculite-based composites have been synthesised with impregnation of different binary and ternary salt mixtures, including V-CaCl₂-MgSO₄, V-MgCl₂-LiNO₃, V-MgSO₄-LiCl, and V-MgSO₄-LiNO₃-MgCl₂. Based on the material characterisation analysis, V-CaCl₂-MgSO₄ exhibits faster kinetics of water release and the highest energy storage density of 121.3 kJ/kg.

The experimental study demonstrated the feasibility of the V-CaCl₂-MgSO₄ composite for low-grade TAHS applications. It required low-temperature operating conditions (i.e., <20 °C) for the adsorption reaction, which is feasible for operation under ambient conditions or requires small input energy. It exhibited fast desorption kinetics under a low-grade temperature range, making it a promising candidate for utilising solar heat or waste heat sources. The V-CaCl₂-MgSO₄ composite showed good cyclic stability, retaining approximately 91.3% of its initial

energy storage density even after 20 charging-discharging cycles. The experimental results demonstrate that the V-CaCl₂-MgSO₄ composite has significant potential as a low-grade thermochemical heat storage material for space heating applications, offering consistent performance over an extended period of use.

The results of this study are promising and suggest the need for further research to scale up the reaction chamber for use in building applications under actual operating conditions. This could involve investigating the composite's performance on a larger scale, as well as assessing its feasibility in a range of different environmental conditions. Furthermore, to address the potential limitations and challenges associated with using composite materials in practical thermochemical heat storage systems, such as slow reaction kinetics, scalability and economic viability, further research is necessary to explore new approaches for optimising the composite material properties. This may include

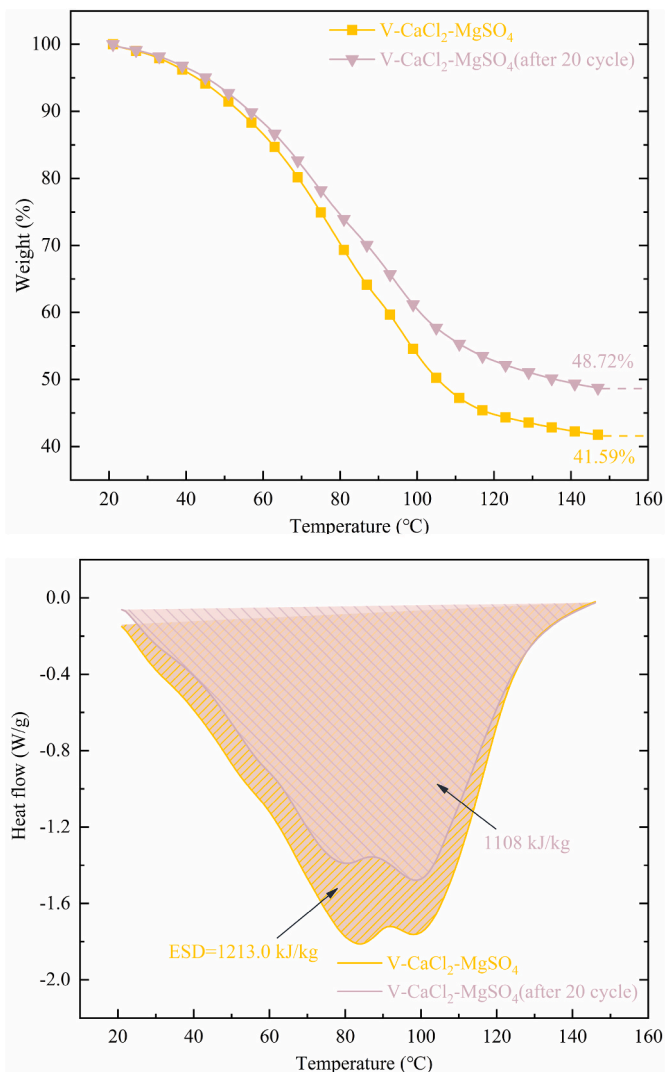


Fig. 12. DSC-TGA results of V-CaCl₂-MgSO₄ composite after 20 cycling tests.

Table 4

Comparison of experimental results with literature findings.

Host matrix	Salt or salt mixture	Number of cycles	Initial ESD, kJ/kg	Final ESD, kJ/kg	References
Vermiculite	MgSO ₄ -CaCl ₂	20	1213	1108 (91.3%)	This study
Vermiculite	LiCl	14	1560	1250 (80%)	[66]
Vermiculite	K ₂ CO ₃	47	2250	1750 (78%)	[45]
Zeolite 13×	MgSO ₄ -CaCl ₂	20	1414.5	1158.5 (81.9%)	[67]
Graphene	MgSO ₄ -MgCl ₂	60	1065.9	968.3 (90%)	[68]
Zeolite	MgSO ₄	6	492.3	401.1 (81.34%)	[69]

improving the synthesis and processing techniques, varying mixing ratio and investigating new composite configurations that may offer improved performance in practical applications.

Credit author statement

Ziwei Chen: Methodology, Investigation, Formal analysis, Writing –

original draft, Writing – review & editing, Yanan Zhang: Conceptualization, Investigation, Formal analysis, Writing – review & editing, Yong Zhang: Investigation, Formal analysis, Writing – review & editing, Visualization, Yuehong Su: Conceptualization, Methodology, Supervision, Project administration, Writing – review & editing, Saiffa Riffat: Supervision, Resources, Project administration, Writing – review & editing.

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

No data was used for the research described in the article.

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