

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]. There are a variety of types of thermochemical heat storage (THS) systems, and thermochemical adsorption heat storage (TAHS) is promising for medium-low temperature applications.

Extensive studies have been conducted 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 [2]. However, salt deliquescence has been regarded as a common issue encountered in salt hydrate-based TAHS systems. To mitigate these issues, researchers have proposed and investigated composite adsorbent materials, which embed hygroscopic salts in a host matrix with a porous structure. The impregnation method is the most used approach to synthesise a composite material. The synthesis conditions can greatly influence the composite properties; therefore, improvements can be made to the impregnation method to maximise the salt content in the composite materials while ensuring composite stability and homogeneity.

In the current work, explorations on optimising the dry impregnation method are conducted, by controlling different parameters during the synthesis process, including the number of impregnation/drying steps, the temperature and concentration of the aqueous solution. Vermiculite is used as the host matrix for incorporating calcium chloride (CaCl_2). The effect of the impregnating parameters on the properties of the resulting composite material is analysed. This help to optimise the dry impregnation method for effectively synthesising improved composite materials with high salt content, high energy density, and cyclic stability for TAHS applications.

Different Approaches for Synthesising Vermiculite- CaCl_2 Composites

In this study, three different approaches are proposed for synthesising the vermiculite- CaCl_2 composite material, namely the conventional dry impregnation method, a multi-step impregnation method, and a concentrated impregnation method.

Dry impregnation uses a salt solution whose volume is equal to or slightly lower than the pore volume of the host matrix. Once the host matrix is contacted 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 drying. The latter two methods are modified on the basis of the traditional dry impregnation method by controlling the parameters (i.e., the number of impregnation/dry steps, the temperature and concentration ratio of the aqueous solution) during the synthesis process.

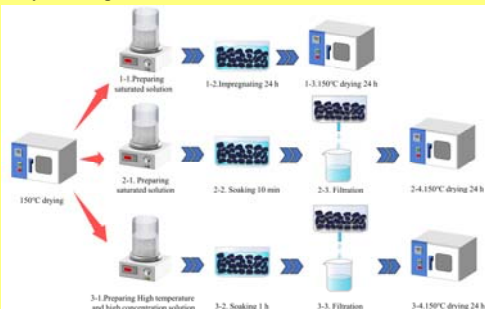


Fig. 1. Illustration of different synthesis procedures

Three different samples of vermiculite- CaCl_2 composite material (VCM) were synthesised, including VCM-1 using the conventional dry impregnation method, VCM-2 using the multi-step impregnation method, and VCM-3 using the concentrated impregnation method. Different techniques were adopted to characterise the three samples, so to investigate the impact of different synthesis parameters on the properties of the resultant composite materials.

Material Characterisation Analysis of Vermiculite- CaCl_2 Composites

Scanning Electron Microscope (SEM) was used to visualise the morphology and microstructure of the synthesised different vermiculite- CaCl_2 composites. An energy dispersive X-ray microanalysis (EDX) system used in this study is Philips (FEI) XL30 SEM. Fig.2 presents SEM photos. The raw vermiculite is highly porous and formed by the accumulation of thin lamellas. The clear layered structure of the vermiculite was still visible for VCM-1 (Fig. 2b), and CaCl_2 was coated onto the lamellas surfaces and embedded in the interlayer spaces. Differently, visible changes in the vermiculite morphology can be noticed for VCM-2 and VCM-3. As observed in Fig. 2(c), VCM-3 failed to display the original layered structure of vermiculite, as salts filled up the interlayer spaces, resulting in the presence of many pores. Although VCM-2 exhibited the contour of the original layered structure (Fig. 2d), it is worth noting that a significant portion of the interlayer spaces has been filled with salts, leading to the appearance of a few pores.

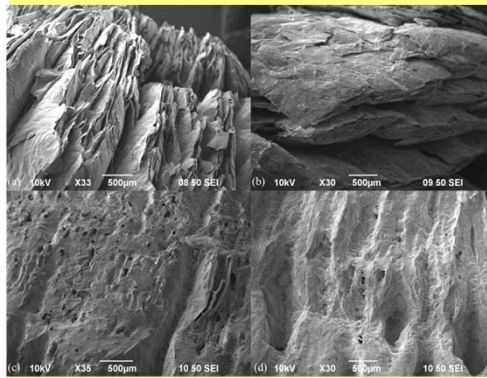


Fig. 2. SEM photos of (a) raw vermiculite, (b) VCM-1, (c) VCM-3 and (d) VCM-2

The salt content of the three samples was examined by Inductively Coupled Plasma Optical Emission Spectrometer. Additionally, the structural properties of the composite samples were also derived through Mercury Intrusion Porosimetry, including the porosity, specific surface area (SSA), and specific pore volume (SPV). Table.1 lists the obtained results. Comparatively, VCM-2 has the highest CaCl_2 content (i.e., 79.14% wt.). By involving multiple impregnation steps, an increase in the salt content of 16% was achieved when compared to VCM-1, which was prepared using the conventional dry impregnation method.

Table. 1. Structural properties and salt content of composite materials

Samples	SPV cm^3/g	SSA m^2/g	Porosity %	CaCl_2 content % wt.
V	4.11	15.10	88.90	0
VCM-1	1.80	32.93	81.94	68.21
VCM-2	0.82	6.96	55.30	79.14
VCM-3	1.01	10.95	69.11	76.19

In this study, the experiment of the moisture vapour adsorption isotherm was conducted in a laboratory incubator with precise and constant environment control (i.e., 40% RH and 20 °C). A saturated solution of magnesium chloride was used for reaching the internal relative humidity level inside the chamber. All the tested samples were completely dried in the oven at 150 °C for 24 hours and cooled down to room temperature in a vacuum seal container before testing.

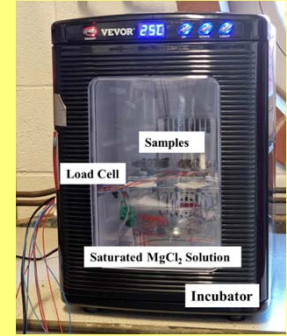


Fig. 3. Photo of test rig

Fig. 4 shows that the water uptake of the composite materials increases with a decreasing growth rate. VCM-1 exhibits a faster water uptake rate, with a water uptake capacity of 0.27 g/g at 20 hours. This is attributed to the higher salt content in the composite material results in decreased porosity and specific surface area, causing an increase in mass transfer resistance.

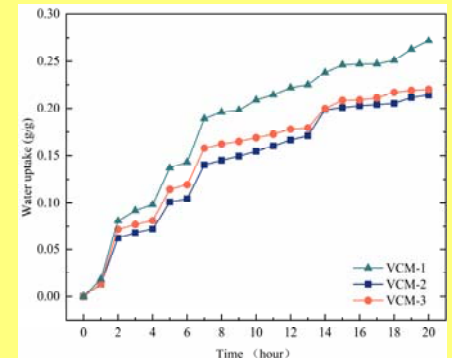


Fig. 4. Water uptake variations of three composites

Conclusions

The results demonstrate that the number of impregnation steps and the concentration of aqueous solution impact the performance of the composite material. Compared to the conventional dry impregnation method, multiple impregnation steps result in a noticeable increase in the salt content of the composite. A high salt content of 79.14wt.% was achieved by involving multiple impregnation steps.

The findings provide useful information on optimising the dry impregnation method to produce composite materials with improved structural and energy storage characteristics for thermochemical adsorption heat storage applications.

Acknowledgement

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References

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- [2] Ting Yan, et al., Performance of thermochemical adsorption heat storage system based on $\text{MnCl}_2\text{-NH}_3$ working pair. Energy, 2022. 239: p. 122327.