Materials characterization of innovative composite materials for solar-driven thermochemical heat storage (THS) suitable for building application

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Abstract

Thermochemical Heat Storage (THS) systems have recently attracted a lot of attention in research and development. One of the main parameters that influence the performance of a THS system is the thermochemical materials. This paper aims to investigate thermochemical materials which are suitable for both short-term and long-term building heat storage application driven by solar energy for an open system. Innovative composite materials using $MgCl_2$-$MgSO_4$, $CaCl_2$-LiCl and $MgSO_4$- $CaCl_2$ salts mixtures impregnated into vermiculite, and potassium formate (KCOOH) impregnated into silica gel will be presented in this study. Initial screening and characterization results of the composite THS materials based on the energy density using differential scanning calorimetry analysis, mass loss against temperature using thermogravimetric analysis, and moisture vapor adsorption isotherms testing are discussed. The characterization analysis suggest that the vermiculite with salts mixtures are promising candidates for thermochemical heat storage (THS) systems compared to composite materials with individual salts. Meanwhile the potential of KCOOH-silica gel as THS materials may be further investigated in the future. The performance of the materials may be further optimized in the future by changing the concentration ratio of the mixed salts.

Keywords: thermochemical heat storage; THS materials; characterization salts mixtures; $MgCl_2$-$MgSO_4$; $CaCl_2$-LiCl and $MgSO_4$- $CaCl_2$ and KCOOH-silica gel; vermiculite

1 INTRODUCTION

Thermal energy storage (TES) plays a pivotal role in synchronizing energy demand and supply, both on a short- and long-term (seasonal) basis. Transformation of our existing building stock towards low energy buildings and nearly zero energy and Plus-energy buildings requires effective integration and full use of the potential yield of renewable energy. Thermal storage is a key priority to make such a step, particularly considering the energy renovation of the existing stock, where compact building level solutions are required. The type of TES systems which have been actively researched and commercially available are the common sensible heat storage (SHS) systems and latent heat storage (LHS) systems. Although SHS is widely used worldwide, low energy density, sizing and insulation are major challenges. PCM LHS of thermal energy, significantly improves energy density, but does not address heat loss. Increasing insulation thickness would help but this increases the size of the system.

Another type of a TES system is thermochemical heat storage (THS). THS systems have major advantages over other thermal storage systems, notably high energy density/low foot print, and low heat loss. Essentially, THS materials can store heat, without losses, as long as they are hermetically sealed to prevent the adventitious ingress of water to the sorbent [1]. Heat will be generated only when water vapor is purposely admitted [2]. This particular aspect allows wider and more flexible usage of THS such as seasonal storage of solar energy for space heating and hot water generation. THS materials were reported to have nearly 8–10 times higher storage density than SHS and double the storage volume basis of LHS materials [1].

Thermal energy storage using renewable sources or waste heat will reduce CO2 emission and lower the need for costly peak power and heat production capacity by replacing the use of fossil fuels. In Europe, the replacement of fossil fuel with renewable sources is estimated to save 1.4 million GWh of power for heat production per year while avoiding 400 million tonnes of CO2 emissions in the building and industrial sectors by more extensive use of heat and cold storage [3]. A THS system for instance can be designed for seasonal (e.g. 4 months) or short-term (e.g. 3–4 days) storage of solar energy. At present, while SHS are commercially available, the PCM LHS and THS-based storage systems are mostly under research and development and demonstration. THS systems in particular need improvements in the stability of storage performance, which is associated with the material properties [3]. This paper is aiming to investigate thermochemical materials which are suitable for long-term heat storage for building application driven by solar energy for an open system. The potential systems will be briefly discussed in the next section. Then, this paper will review THS materials, of which the published literature on thermochemical materials using salts mixture impregnated into host matrices being the main interest of the present research. Aiming to optimize the performance of THS materials, this paper discusses innovative nano-composite materials or salts in matrix (SIM) using $MgCl_2$-$MgSO_4$, $CaCl_2$-$LiCl$ and $MgSO_4$- $CaCl_2$ salts mixtures impregnated into vermiculite as a host matrix. Meanwhile the use of KCOOH impregnated into silica gel as a potential THS materials are also explored and discussed in this paper. The scope of the discussion has been limited to the characterization analysis of the composite materials. Initial screening and characterization analysis are vital in determining the potential of the proposed composite materials to be used in the proposed THS system, driven by solar energy.

2 SOLAR POWERED THS

The selected thermochemical materials investigated in this study can be used for both domestic and commercial buildings (such as houses, schools, offices), and also for greenhouses. Where none of these options are available, heat storage tanks could be placed underground externally. The concepts of the charging and discharging processes are described in Figure 1 and the operational steps are described in Table 1. Aiming for open seasonal heat storage application, the developed 'seasonal' heat storage system will have significant impact on reducing fossil fuel consumption for space and water heating. In charging mode (Figure 1), the solar heated dry air from the solar collector will desorb the moisture from the wet composite material. When the climate does not require space heating, the moist and warm outlet air transfers heat to the hot water cylinder via an efficient air-to-water heat exchanger. The charged (fully dried) sorbent is then stored dry, separate from the humidification unit for use in the next system discharge cycle. The system will be controlled via a set value of solar radiation. In discharging mode, the warm air from the solar collector will be humidified using a humidifier and the moist outlet air will enter the modular heat storage tank. As a result of the vapor sorption process, heat will be generated (Figure 1). Transferring heat to the building efficiently is important for maximizing system performance. In doing so, a commercially available fan coil could be used.

For the intended application, among the main parameters that influence the performance of a THS is the choice of
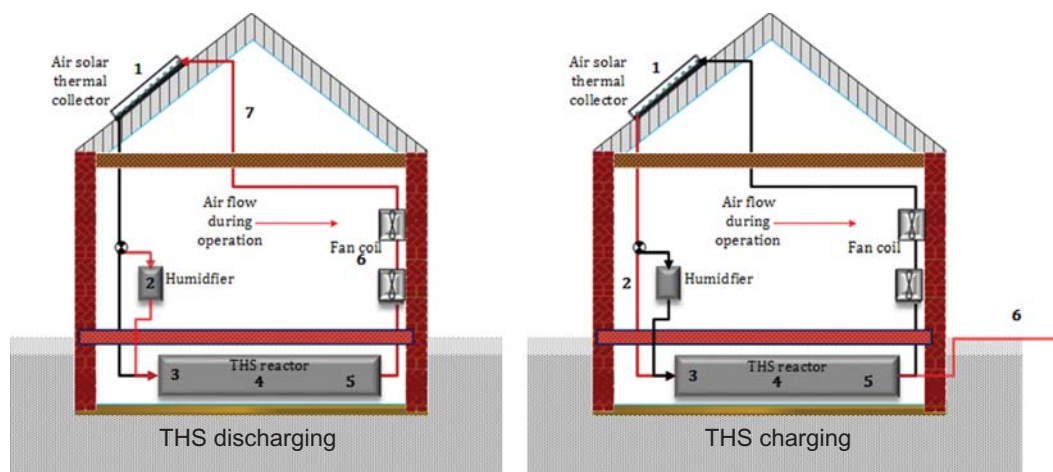

Figure 1. *The concepts of the charging and discharging processes for THS.*

Table 1. *Operational steps for the charging and discharging processes.*

Discharging	Charging
1-Air is preheated in solar air collectors (20–25°C)	1-Air is heated in solar air collectors (80–100°C)
2-Air is humidified (The target RH is approximately 60–80%)	2-By-pass line is used and air is not humidified in this process
3-Humid air enters the THS	3-Hot dry air enters the THS
4-Heat is generated whilst vapor is absorbed by the sorbent (45–55°C)	4-The hot air is transferred to the sorbent and moisture is released by the sorbent
5-Hot air is collected with an outlet duct	5-Warm, humid outlet air is collected with a duct
6-Heat is transferred to the building with fan coils	6-Exhaust air is released to the ambient
7-Air returns back to collector and cycle is completed	

thermochemical materials [2]. In selecting the appropriate materials, key considerations include: high energy storage density, low charging or regeneration temperature of which regeneration temperature of 80°C is favorable, high water or sorbate uptake as measured in (g sorbate/g sorbent), appropriate heat and mass transfer properties for efficient power output, ease to handle and non-poisonous nature, low-cost price per kW/h of energy stored with thermal stability and suitability for the application. This study is crucial in identifying suitable materials that can be applied for storage application. Thus, the following sections of this paper will discuss the results from the initial screening of the proposed innovative materials based on materials characterization analysis.

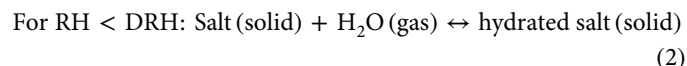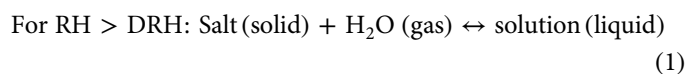## 3 CURRENT STATE OF THE ART OF THS MATERIALS

As discussed in Yu *et al.* [4], the sorption pair for a sorption thermal storage may be categorized into four important categories: (i) liquid absorption; (ii) solid adsorption; (iii) chemical reaction; and (iv) composite materials. In solid adsorption, the reactions are typically exothermic. A good material should have high surface area with proper pore structure, good mechanical strength and stability, and low regeneration temperature (less than 120°C) [4]. The most common examples of solid adsorption materials are Silica gel/H_2O [5, 6], zeolite 13X/H_2O [7], zeolite 13X [8], zeolites [9, 10], SAPO, a dealuminated faujasite type zeolite, and a mesostructured aluminosilicate [11], and molecular sieves-synthetic zeolites [11, 12].

Metal organic frameworks (MOF) are new adsorbent materials which have received a lot of attention by researchers in various fields of sorption/separation application including storage system. Additionally, among the most recent research on MOF includes water harvesting application [13]. In a thesis by LANGE [14], in addition to its high surface area and pore volume which gives high adsorption uptake, it is reported that MOF may perform better than the commercially used zeolites, activated carbon or silica gels due to the structures of MOF that can be selected and further tuned in optimizing their adsorption characteristics for specific application. According to the author, currently more than 20 000 MOF structures are known [14, 15]. For energy storage application, MOF may be considered as an emerging materials, thus, there is only a small number of research have been published and

a very limited information on the performance of MOF compared to conventional adsorbents such as zeolites, silica gel and activated carbons [16]. Furthermore, although MOF materials have been commercialized alongside zeolites, silica gel, etc., the efficiency of the materials have a potential to be further improved in terms of the optimization of adsorbents [17]. Reported in Ref. [17] focusing on adsorption heat transformation application, among the MOF materials which has high adsorption and stability criteria [15] are CAU-10-H (CAU—Christian-Albrechts-Universität) [18] which plays a highly suitable step-wise water adsorption behavior for application in adsorption-driven heat pumps and chillers, 23 types of MOF of which the permanent porosity of all 23 materials was confirmed and MOF-801-P and MOF-841 show the highest performance such that they are 'water stable, do not lose capacity after five adsorption/desorption cycles, and are easily regenerated at room temperature' [19].

For liquid absorption, among the THS materials being researched are hygroscopic inorganic salts such as LiCl [20], LiBr and $MgCl_2$ [21], $MgSO_4$ [4, 22], $LiNO_3$ and $SrBr_2$ [23]. Hygroscopic salts such as $MgCl_2$, LiCl, Na_2S and $MgSO_4$ are more promising compared to traditional liquid sorbents such as silica gel and zeolite due to high energy densities. However, these salts suffer a severe problem known as deliquescence, in which hygroscopic salts become saturated at certain relative humidity (RH) levels. LiCl/H_2O, for instance, has been identified as the best sorbents due to its high energy density. However, the sorbent suffers severe problems due to liquid solutions produced after a few cycles [24]. Additionally, phenomena such as swelling and agglomeration must be taken into account, since they may cause unwanted obstacles to the mass transfer which would lead to a decrease in the charging and discharging rate [4].

In a THS system which uses salts as the thermochemical materials, deliquescence relative humidity (DRH) values are of interest, as they indicate the sorption properties of the THS materials. As comprehensively discussed in Ref. [25], presented in equation (1) is the process whereby the environment reaches the value of deliquescence relative humidity (DRH) or above. At this stage, deliquescence of the salt will occur since the inorganic salts will absorb moisture from humid air and form a solution. Meanwhile, when the value of the relative humidity is below the DRH, the salt may still absorb moist or water vapor, thus becoming hydrated, but it will not create solution. This is described in equation (2) as given in Ref. [25]:

For RH > DRH: Salt (solid) + H₂O (gas) ↔ solution (liquid)

$$\text{For RH} > \text{DRH: Salt (solid)} + H_2O \text{ (gas)} \leftrightarrow \text{solution (liquid)} \tag{1}$$

$$\text{For RH} < \text{DRH: Salt (solid)} + H_2O \text{ (gas)} \leftrightarrow \text{hydrated salt (solid)} \tag{2}$$

This thermochemical reaction is a reversible process. Thus, in both reactions presented by (1) and (2), the total amount of heat generated/absorbed during the reaction is given by the latent heat of condensation/evaporation and the thermochemical reaction during the water sorption/desorption process. However, the formation of salt solution in equation (1) implies that a higher amount of heat is generated compared to reaction of equation (2) during the sorption reaction due to the additional water sorption of the THS materials. Similarly, during desorption, if the salt used is in a liquid state, higher enthalpy change is required to regenerate the salt. Although higher energy is produced during the discharging (sorption) stage, the second process suffers from a disadvantage caused by the salt solution possibly affecting the hosting materials [25].

In tackling issues in regard to deliquescence of the salt during hydration, recent research in THS has led to innovations in composite materials which combine salts and host matrix, or salt in matrix (SIM) [26]. The composite materials generally meet all the requirements of excellent TES materials in improving sorption properties [2]. This concept was originally introduced by [27–29], who investigated the use of composite materials which may be applied in various types of sorption applications including cooling, heating, and storage applications. For materials in which water is the sorbent, the composite materials are known as Selective Water Sorbent (SWS).

Another important property of the salts during the sorption reaction process is the hygrothermal stability of the salts as indicated by DRH values. This property implies the rate of hydration reaction. For example, although the solution of MgSO₄·7H₂O has high dehydration enthalpy, the DRH values of MgSO₄ at 30°C is 90% [30], which indicates that the anhydrous MgSO₄ reacts very slowly with water vapor to reach its hydrous state (MgSO₄·7H₂O) °C. The salt should not be able to take up water at temperatures above 40°C [31].

Thus, an innovative approach has been made by some researchers in applying mixture of salts into host matrices in reaching a balance between the enthalpy capacity and the hydration rate (discharging rate) process of the thermochemical materials. For example, Posern and Kaps [25], investigated the inorganic MgSO₄-MgCl₂ salts mixture in an Attapulgite Granule host matrix. In their study, Posern and Kaps chose the salts mixtures due to the significant difference in the DRH values of each of the salts. Characterization analysis was performed to investigate Attapulgite granulate impregnated with mixtures of MgSO₄ and MgCl₂ hydrates for suitability as a composite thermal energy storage material. Using the isothermal heat of sorption and thermo-gravimetric (TG) materials characterization method, the proposed materials were tested to check their suitability as THS materials. In their research they concluded that the salt mixtures behaved differently than pure MgSO₄. The reduction of the DRH values of the mixture via partial substitution using MgCl₂ led to the increase in the condensation capacity, thus increasing the heat generated and released. Also, the energy density of the composite heat storage material containing a salt mixture of 20 wt% MgSO₄ and 80 wt% MgCl₂ was measured as 1590 kJ/kg and occurs at 30°C/85% RH. These values were obtained at desorption temperature of 130°C.

In a different study, Posern and Kaps [32] carried out a material characterization of composite materials using open porous glass pellets with pore sizes from 45 nm to 40 µm with magnesium sulfate and salt hydrate mixtures of MgSO₄-MgCl₂ and MgSO₄-LiCl in different ratios. The mixtures of both salts showed promising results. By partially substituting the MgSO₄ with 40 wt % MgCl₂ and 20 wt% LiCl, at 30°C temperature and 85% of RH the heat of sorption of MgSO4 which was initially measured as (2300 J/g) increases to 5290 J/g and 5400 J/g, respectively. The results imply that the sorption heat of the salt hydrates was enhanced due to the introduction of the salts mixtures. Druske et al. [20] investigated an innovative mixtures of CaCl₂ and KCl impregnated into host matrices including activated carbon foam media, compacted expanded natural graphite and expanded natural graphite powder. The composite THS materials were investigated as materials for developing of the heat storage system known as a 'thermal battery' suitable for domestic and industry applications. From the energy density properties analysis, the associated thermochemical reactions show great potential for high energy density and long-term storage applications.

Recently, a group of researchers [33] have investigated the performance of composite Vermiculite with CaCl₂-LiNO₃ salt mixture. In their study, alongside Vermiculite-CaCl₂ and desiccant Zeolite 13X, all the materials were experimentally investigated for suitability to be applied for domestic scale thermal energy storage. In doing so, a 3 kWh thermochemical reactor were built to examine the performance. Due to the property of CaCl₂ which has a high sorption rate, the salt is mixed with LiNO₃ which has a slow response to moisture and low sorption rate. The researchers aimed to lower the desorption temperature and increase the moisture sorption-desorption stability of CaCl₂. However, the researcher found out that the sorption rate remained low since the LiNO₃ dominated the new composite perhaps due to the mixing ration used. The researchers have concluded that using CaCl₂ individually as THS material is more effective and advantageous.

Researchers such as Rammelberg et al. [34] have investigated thermochemical materials involving salts mixtures without impregnation into host matrix. They have examined the stability, enthalpy, and mass balances of MgCl₂, CaCl₂ and MgSO₄. The mixture of CaCl₂ and MgCl₂ showed good cyclability and superior kinetic properties compared to the performance of individual salts. However, the scope of this paper is to investigate the performance of composite materials with salts mixtures.

4 MATERIAL SELECTION AND SYNTHESIS

4.1 Innovative composite materials of vermiculite impregnated with $MgSO_4$-$MgCl_2$, LiCl-$CaCl_2$ and $MgSO_4$-$CaCl_2$

The targeted salts within the proposed studies are $CaCl_2$, $MgCl_2$, LiCl and $MgSO_4$ and their mixtures in various compositions. These salts are highly hygroscopic. Their reaction with water vapor is exothermic as the hydration energy exceeds their lattice energy with heat released. These salts are deliquescent and will dissolve without proper containment within a host matrix. As discussed in Section 3, the DRH value of the materials is very important to indicate the reaction rate of the salts during hydration (discharging of TES process). The DRH values and some of the properties of each salt solution used in this research as cited from existing literature are summarized in Table 2.

Individually, $MgSO_4$ has a high energy storage density (>0.8 MJ/kg), however its slow sorption kinetics remains as the main barrier to utilize this material in THS systems. On the other hand, despite its high energy storage density and fast sorption kinetics, high regeneration temperature (>150°C) is a disadvantageous aspect for $MgCl_2$ to be used for solar heat storage. For that reasons combination of $MgCl_2$-$MgSO_4$ was proposed to contribute to the progress towards development of optimum THS materials.

$CaCl_2$ has been widely researched by the authors [1, 2, 26] previously. It was found as a promising candidate in terms of sorption rate, heat storage capacity, hygrothermal performance and cyclic ability. The main weakness of this material was found to be unsteady thermal performance during discharge. Due to its fast sorption kinetics, it initially releases a high amount of sorption heat, dropping sharply in the following period. During the process, reaction front becomes wet in short period of time, preventing air flow and causing a pressure drop. Optimizing the sorption kinetics of $CaCl_2$ is crucial to enhance the performance of this material. For that reason, combining this salt with LiCl ($CaCl_2$-LiCl) that has relatively steadier hygrothermal performance was proposed.

From Table 2, although $CaCl_2$, possesses high energy density, the DRH value is rather low in comparison to $MgSO_4$. The mixture of $MgSO_4$-$CaCl_2$ impregnated into vermiculite was also investigated. The aim is that the mixing of both salts will result in an increase in the overall energy density and lowering the DRH value of $CaCl_2$ at a given temperature level.

Table 2. *DRH values of $CaCl_2$, $MgCl_2$, LiCl and $MgSO_4$ as reported in the literature.*

No	Thermochemical materials	DRH value
1	$MgSO_4$	92% at 25°C [32]
2	$MgCl_2$	33% at 25°C [32]
3	LiCl	11% at 25°C [32]
4	$CaCl_2$	19–24% and 28.1% at 25°C [35]

SIM composites were synthesized using the Insipient Wetness Technique (IWT) method [1]. The technique utilizes a dry porous material's natural liquid absorption capacity (i.e. capillarity) to fill the pore structure with a desired salt solution.

For the composite materials discussed in Section 3, although some researchers have investigated the potential of using $MgSO_4$ and $MgCl_2$ as a salt mixture impregnated into host matrices, none have used vermiculite in their host matrices. The use of vermiculite as a host matrix impregnated with a single type of inorganic salt such as $LiNO_3$, $CaCl_2$, $MgSO_4$, LiCl, $MgCl_2$ and LiBr has been previously investigated by the authors in Refs [1, 2, 26]. From a detailed characterization analysis conducted by Casey *et al.* [2] of a composite material with $CaCl_2$ as the salts solution, N_2 physisorption analysis suggests that materials such as silica gel, activated carbon and zeolite 13× as the host matrix show damage, while the composite materials in the vermiculite samples do not show any damage. The addition of salt into the non-vermiculite host matrix have reduced the ratio of the mesopore volume to total volume, which limits the absorptivity of the moisture vapor. Additionally, as reported in Ref. [1], vermiculite may be considered as an excellent candidate for a host matrix due to its low regeneration temperature (50–80°C) and low-cost (0.21–44 $/kg). The low regeneration (charging) temperature of vermiculite is appealing, since such a temperature is achievable in a conventional solar collector. Additionally, the macro porous nature of vermiculite offers an ideal host matrix for salt impregnation, overcoming the issue of the deliquescence of the salts. One unique feature of salts confined to a host matrix is that they consist of two components, namely a porous host matrix and an active salt inside the matrix's pores. Variations of the components' nature and content allow target-oriented synthesis of a composite adapted to the desired climatic conditions. While vermiculite has a small level of potential sorption energy due to its high specific surface area, in this case it is used strictly as a host matrix in the composite material, inhibiting deliquescence of the salt and preventing any salt leakage during the THS cycling operations.

The current research work is classified into sample preparation (material synthesis); and the characterization of the proposed materials, which includes comparisons between the bulk and solid density, porosity, desorption kinetics, energy density of the materials and the moisture vapor adsorption capacity of the innovative materials.

The composite materials are known as salt in matrix (SIM). The technique used to synthesize the SIM's was based on the methods pioneered by Prof. Yuri Aristov at the Boreskov Institute of Catalysis, Novosibirsk, Russia [27]. As described in detail in our previous publication [2], based on the selected composite materials, the following steps have been followed in synthesizing the materials:

(1) The first step includes the determination of the specific pore volume, V_p of the matrix material (cm^3/g). This can be obtained using Mercury Intrusion Porosimetry (MIP) device. In this study, the value of V_p for Vermiculite was determined as 2.84 ml/g.

(2) The second step is to measure the total sample mass (mm). Note that for a saturated salt solution of approximately 100% of the matrix pore volume, the total amount of saturated solution was then prepared as given by mm x V_p.

(3) The third step is mixing the saturated salt solution with the host matrix, e.g. vermiculite. Attention should be given during the mixing of the solution with the dried vermiculite (host matrix), such that the solution is added into the host matrix in a container while being constantly stirred. Note that through capillary action, the matrix will be soaked by the saturated solution. In this step, the mixed materials still appear dry.

(4) The fourth step is to ensure that the matrix has been uniformly impregnated by the salts. The mixing of the solution with the matrix should be complete as verified via visual confirmation such that a fully wetted transition occurs.

(5) The final step is to dry the wetted SIM. In order to dry the wetted SIM, the SIM is placed in an oven to evaporate the water and in order to ensure that the salt within the matrix is entrapped. A minimum of $T = 150°C$ must be set as the drying temperature to achieve full dehydration of the impregnated salt.

(6) The mass of salt impregnated into the matrix (as %) is calculated as the change in the mass after drying as shown in equation (3). Here, m_{SIM} and m_v indicate the mass of anhydrous SIM composite and raw vermiculite, respectively:

$$m_{salt} = \frac{m_{SIM} - m_v}{m_{SIM}} \times 100(\%). \qquad (3)$$

The mixtures of the salt solutions of $CaCl_2$, $MgCl_2$, LiCl and $MgSO_4$ being investigated in this research were mixed in certain mixing ratios as summarized in Table 3. The proposed salt mixtures ($MgSO_4$-$MgCl_2$, LiCl-$CaCl_2$ and $MgSO_4$-$CaCl_2$) were prepared by mixing equal volume of saturated salt solutions.

The mass and volumetric ratios of salts in the mixture solution have been determined based on their molar mass, density, and solubility in water as presented in Table 4. The volumetric and mass ratios of salts in $MgSO_4$-$MgCl_2$ mixture were calculated as (6.59 ml MgSO + 11.70 ml $MgCl_2$) and (17.55 gr $MgSO_4$ + 27.15 gr $MgCl_2$) per 100 ml water, respectively. Meanwhile, volumetric and mass ratios of salts in LiCl-$CaCl_2$ mixture were calculated as (10.29 ml LiCl + 17.32 ml $CaCl_2$) and (21.20 gr LiCl + 37.25 gr $CaCl_2$) per 100 ml water, respectively. Similarly for $MgSO_4$- $CaCl_2$ volumetric and mass ratios of salts in mixture were calculated as (6.59 ml MgSO + 17.32 ml $CaCl_2$) and (17.55 gr $MgSO_4$ + 37.25 gr $CaCl_2$) per 100 ml water, respectively. During the preparation of materials, as the saturated mixtures of the salts has mixed, no change has observed in temperatures. Therefore physical property at room temperature (25°C) was considered for each salt during synthesize of the mixtures as presented in Table 4.

To confirm the presence of the salts, visual affirmation is necessary. In this research, an environmental scanning electron microscope (SEM) equipped with a field emission gun has been

Table 3. *The mixing ratios of the salts mixture.*

No	Mixture type	$MgSO_4$	$MgCl_2$	LiCl	$CaCl_2$
1	$MgSO_4$-$MgCl_2$	50%	50%		
2	LiCl-$CaCl_2$			50%	50%
3	$MgSO_4$- $CaCl_2$	50%			50%

Table 4. *Physical properties of salts.*

	$MgSO_4$	$MgCl_2$	LiCl	$CaCl_2$
Molar mass (g/mol)	120.3	95.2	42.4	110.9
Density (g/cm^3)	2.66	2.32	2.06	2.15
Solubility @25°C (g/100 ml)	35.1	54.3	42.4	74.5
Solubility @25°C (ml/100 ml)	13.2	23.4	20.6	34.6

used to obtain the images of which some of the examples are shown in Figure 2.

4.2 Innovative composite materials of Potassium formate (KCOOH) impregnated with silica gel

In this study, a new composite material using potassium formate (KCOOH) impregnated with silica gel as the candidate materials for thermal heat storage is explored. The use of silica gel is well known in THS application due to its low-cost and low-desorption temperature [4]. However, for potassium formate the research in adsorption has mainly being applied as desiccant materials of which among the earliest study was conducted by [36] on the small-scale absorption chiller test rig. KCOOH has also been applied as a desiccant in a packed column [37], in a rotor impeller absorber [38], a liquid desiccant cooling system driven by the flue gas waste heat of a biomass boiler [39], in an innovative liquid desiccant dehumidification system with a counter-flow heat and mass exchanger (numerical study) [40], A Novel SOFC Tri-generation System for Building Applications, and in a novel integrated desiccant air conditioning system (IDCS) [41]. Reported in Ref. [41] when compared to halide salts, KCOOH is a weaker desiccant than the halide salts. However its ability to dehumidify air below 30% relative humidity and its favorable physical characteristics makes it an attractive option for building air conditioning applications. From literature the advantages of KCOOH as an adsorbent may be summarized as follows:

(i) Low-cost/cheap in comparison to the typical desiccant such as $CaCl_2$ and LiCl [37, 40].

(ii) Environmentally friendly-non-corrosive 'non-toxic, biodegradable and environmentally responsible in case of spillage or accidental release' [36].

(iii) It has a negative crystallization temperature [38] high solubility (up to 80% at ambient temperature) and gives consistent humidity reduction [36, 37, 41].

(iv) Desiccant regeneration requires a temperature level around 40–50°C which can be easily obtained by using solar energy or heat recovered from an industrial process or from a thermal engine [37].

The synthetization of KCOOH and silica gel, which has been performed by the researchers at Nottingham University, UK involves the following steps:

Step 1: 1 l of KCOOH saturated solution was dried in the oven at 150°C for 72 h to turn the solution into a powder form (see Figure 3(a)).

Step 2: 460 g dried KCOOH powder was then prepared to be mixed with Silica gel (see Figure 3(b)).

Step 3: At ratio 2:1, 230 g of silica gel was grinded into powder form and mixed with the KCOOH powder (see Figure 3(c)).

Step 4: To impregnate the KCOOH into the silica gel, the mixture was left in the container for 7 days until the materials turned into a 'sticky' or 'viscous solution' form (see Figure 3(d)).

Step 5: The mixture was then dried in the oven at temperature 150°C to complete the impregnation process.

5 MATERIALS CHARACTERIZATION ANALYSIS

Characterizations of the sample materials for both hygrothermal properties and pore structure were conducted using advanced characterization tools and devices. Characterization analysis includes solid and bulk density measurement, energy density using differential scanning calorimetry (DSC) analysis and mass loss against temperature using thermo-gravimetric analysis (TGA).

5.1 Energy density using DSC analysis and mass loss against temperature using TGA

Energy storage density E_d (kJ/kg) is the most important material property. DSC of with a TA Instrument SDT Q600 was used to determine E_d. Prior to testing, the wet sample of the composite materials was put in a sealed chamber at RH of 95% at temperature of 23°C since the test should be performed under a room temperature condition as a start. After 48 h, the equilibrium condition was achieved and the specific moisture content of the materials reached RH 95%. For each set of tests, within the temperature range of $30 < T < 140$°C, a baseline analysis was taken using two empty alumina pans (of TA instrument: T1605906) at a heating rate of 10°C/min. The measurement principle may be described based on the specific heat capacities difference between the reference (empty alumina pan) and the SIM sample, which leads to a temperature difference. The heat flux difference is given based on this temperature difference. All the SIMs were tested three times and the mean values of E_d were then calculated. Figure 4 is the examples of the graph of heat flow against temperature obtained from the DSC measurement for the following SIMs: V-MgCl$_2$-MgSO$_4$, V-CaCl$_2$-LiCl and V-MgSO$_4$-CaCl$_2$. Using the function 'tools' available in the Universal Analysis Software 2000 by TA instrument [42], the results were subtracted with the results obtained from the baseline analysis. By integrating the area under the curve using the 'analyze-running integral' function, the energy density of the composite material was computed.

From the characterization analysis, as shown in Figure 5, without taking KCOOH-silica gel into consideration, the calculated values of energy density of SIMs with the mixed salts is
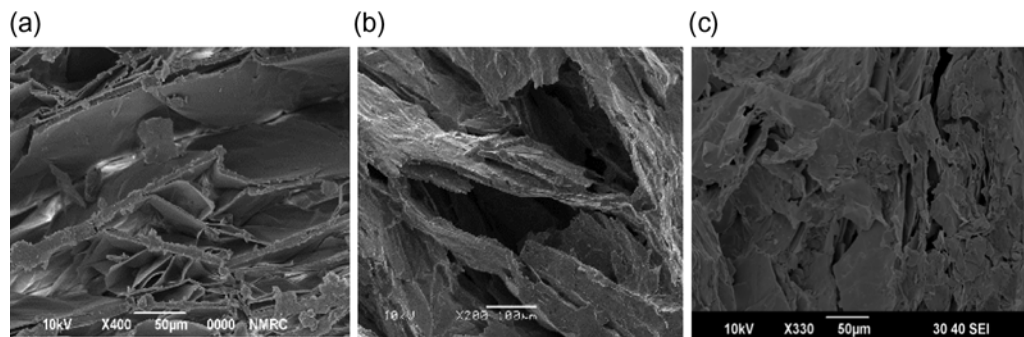

Figure 2. *SEM micrographs of (**a**) Vermiculite, (**b**) Vermiculite-CaCl$_2$-LiCl, (**c**) Vermiculite-MgSO$_4$-MgCl$_2$.*
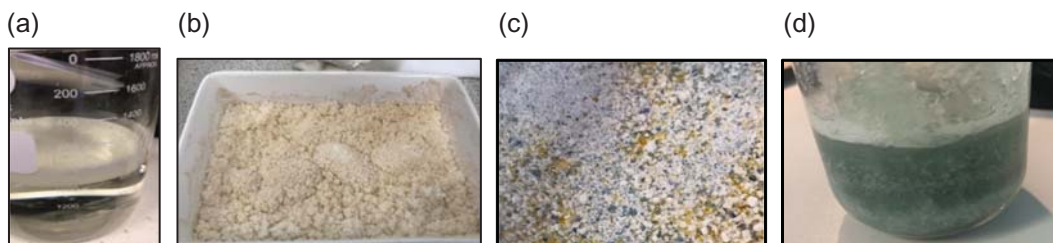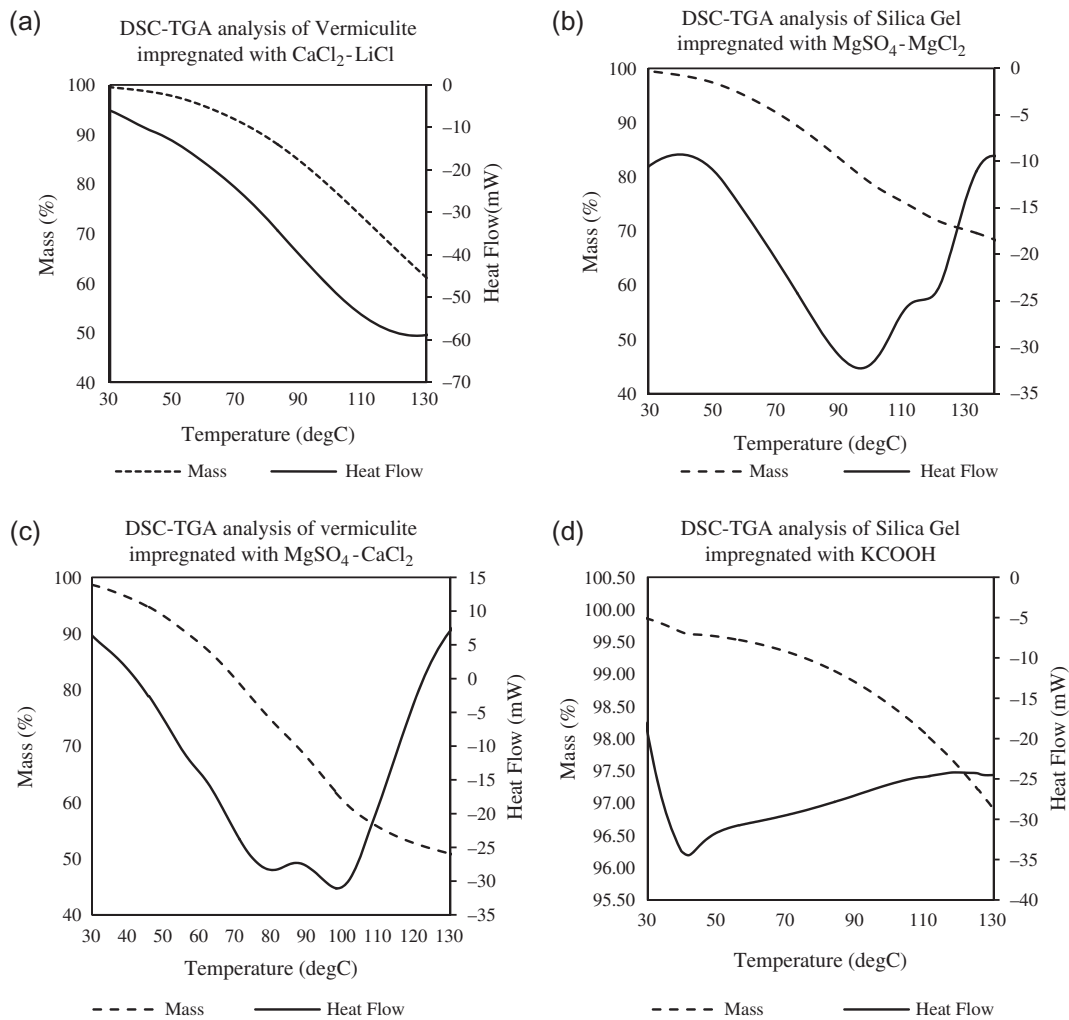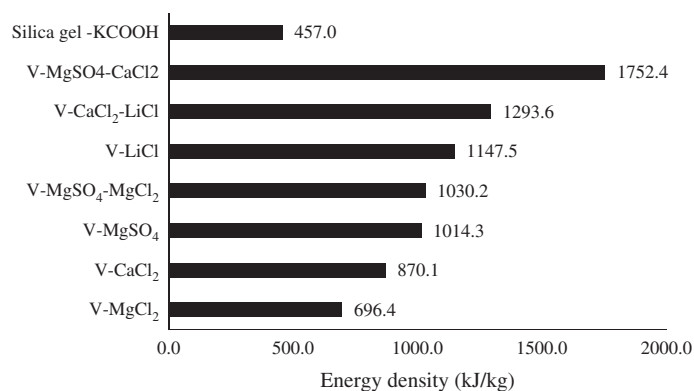

Figure 3. *(**a**) KCOOH solution (**b**) dried KCOOH in powder form (**c**) mixed KCOOH powder and silica gel powder and (**c**) KCOOH impregnated into silica gel in sticky solution.*

Figure 4. *Thermo-gravimetric (TG) and DSC plots for the (a) V-CaCl$_2$-LiCl sample, (b) V-MgSO$_4$-MgCl$_2$ sample, (c) V-MgSO4-CaCl2 sample and (d) Silica gel-KCOOH sample.*

Figure 5. *The energy density analysis for the investigated composite materials.*

higher compared to SIMs with individual salt. SIMs which are impregnated with individual salts; V-LiCl displayed E_d of 1147.50 kJ/kg, meanwhile SIM of V-CaCl$_2$ displayed E_d of only

870.1 kJ/kg, which is almost 300 kJ/kg lower than SIM of V-LiCl. In order to potentially maximize the adsorption potential of the salt-based sorbent, both salts were combined to give composite material of (CaCl$_2$-LiCl) salt based, which then gives E_d of 1293.6 kJ/kg, higher than the SIMs of individual salt. The energy density of vermiculite with MgSO$_4$ alone was found at 1014.3 kJ/kg. When mixed with, MgCl$_2$ the E_d obtained for the SIM with the impregnated salts mixture is slightly higher such that the measured energy density is 1030.2 kJ/kg. However, when mixed with CaCl$_2$, there is a significant increase in the E_d to as high as 1752.4 kJ/kg. The lowering of DRH values of MgSO$_4$ due to partial substitution with CaCl$_2$ leads to higher amount of evaporation heat during the liquid-gas-solid reaction in the SDT device. For storage application, the potential of KCOOH impregnated into silica gel was also investigated. From the DSC analysis, the measured energy density for KCOOH-Silica gel was found as 457 kJ/kg. Although the performance of vermiculite impregnated with salts mixtures or some individual salts on average are at higher values, these

materials are prone to corrosion and salts such as LiCl and CaCl2 are high in cost. Thus, the potential of KCOOH as THS materials of which cheaper, non-corrosive and environmentally friendly is worth to be explored and optimized in the future.

A TA Instrument SDT Q600 analyzer was also used to perform TGA on the tested materials. The wet samples began to lose water as soon the device was set to run. The results are shown in Figure 6. For the case of $MgSO_4$ and $MgCl_2$, the composite materials with the impregnated mixed salts displayed the highest mass loss (60%) within the specified temperature range in comparison to the composite material with individual salts. A similar curve has been obtained for the case of composite materials with $CaCl_2$ and LiCl. For THS materials using vermiculite impregnated with of $MgSO_4$ and $CaCl_2$, when compared to other THS materials impregnated with mixed salts, at temperature of 60°C, the material has demonstrated the highest amount of mass loss which implies that among all other materials, vermiculite with $MgSO_4$ and $CaCl_2$ may have the lowest regeneration temperature. Meanwhile for KCOOH-Silica gel, the amount of mass loss is significantly small which is less than 5% within the same temperature range used for other materials being tested. TGA analysis is important since it provides an overview of the hydration rate of the composite materials. A higher rate of water vapor adsorption implies higher rate of water loss for a given temperature range.

From the TGA-DSC analysis, when 50% of $MgCl_2$ is substituted with $MgSO_4$, 50% of $CaCl_2$ is substituted with LiCl, and 50% of $MgSO_4$ is substituted with $CaCl_2$ the mixture of salts reduces the desorption temperature of the composite THS materials, perhaps due to the recreated weaker chemical bonds between salt and water molecules. As a result, a higher rate of heat mass loss or dehydration rate for the composite materials or SIM was obtained from the TGA analysis when compared with the use of salts without mixing. The lowering of DRH values of $MgSO_4$ due to partial substitution with $MgCl_2$ and $CaCl_2$ leads to higher amount of evaporation heat during the liquid-gas-solid reaction in the SDT device. Meanwhile, for $CaCl_2$ and LiCl, the difference in the DRH values of both salts are not very significant which explains the small difference in the amount of mass loss of the mixed and non-mixed composite materials. Despite the effect of mixing $CaCl_2$ and LiCl on desorption kinetics being minimal, a substantial increase on energy density was obtained with the $CaCl_2$-LiCl mixture. This may be due to the reformation and recombination of salts
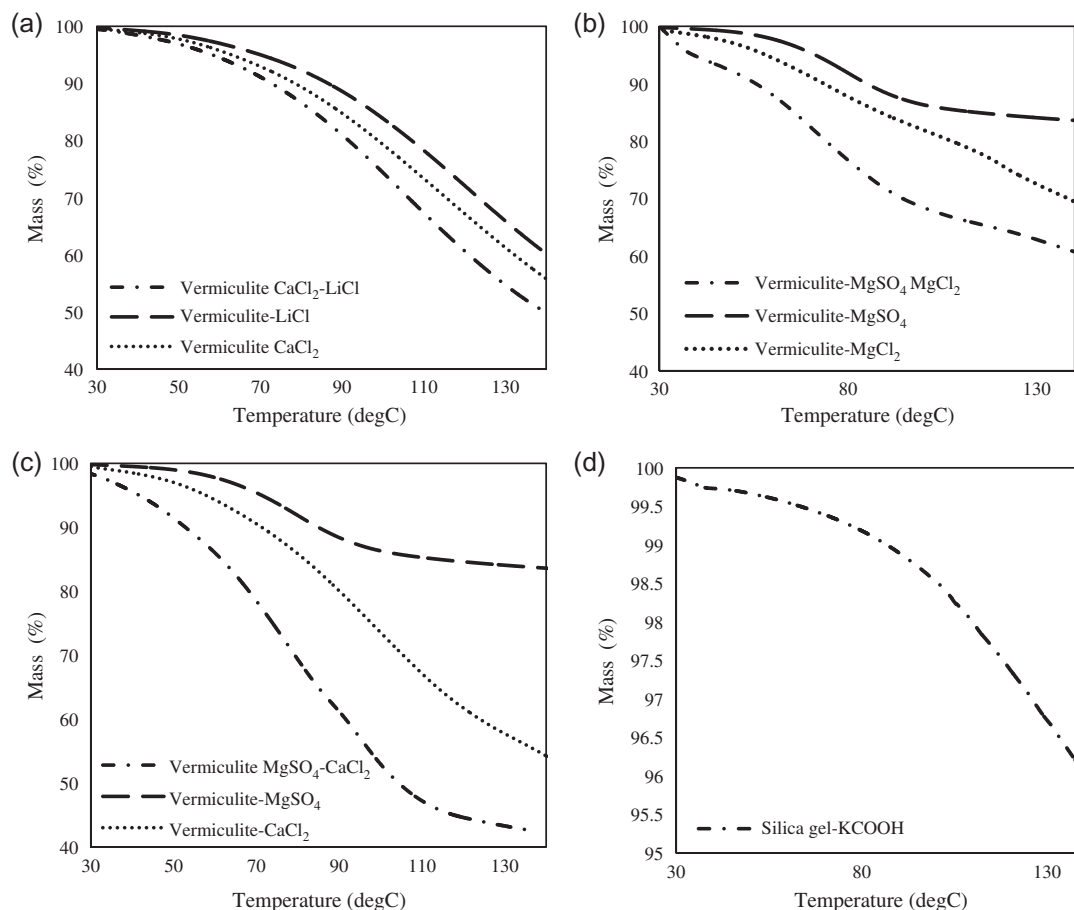
Figure 6. *(a) Thermo-gravimetric plots and for vermiculite impregnated with individual and mixed salts of $CaCl_2$ and LiCl. (b) Thermo-gravimetric plots for vermiculite impregnated with individual and mixed salts of $MgSO_4$ and $MgCl_2$. (c) Thermo-gravimetric plots for vermiculite impregnated with individual and mixed salts of $MgSO_4$ and $CaCl_2$ and (d) the Thermo-gravimetric plots for the SIM with silica gel-KCOOH.*

during water sorption process, releasing a higher amount of sorption heat.

5.2 Moisture vapor adsorption isotherms

The moisture vapor adsorption isotherms for all materials were determined by gravimetric dynamic vapor sorption (DVS) in accordance with BS EN ISO 12 571 which is similar to the previous work conducted by some of the current researchers [2]. A custom built successive desiccator chamber system as shown in Figure 7 was used to control internal relative humidity (RHie) and T at 23°C to an accuracy of ± 1°C. The internal RHie shows difference in four boxes provide an information about different water uptake of test materials. The 3139 Micro Load Cell (0–100 g) was used to measure the change in mass of the composite materials or SIMs with time. The electrical signal output by the load cell is very small and requires specialized amplification. Thus, datataker 85 was used for the amplification and measurement of the electrical output.

For this test, the relative humidity in the chamber was maintained at RH ~16%, 40% 75% and 92% by placing lithium chloride, magnesium chloride, sodium chloride and potassium nitrate saturated solution in the airtight chamber (a) to (d), respectively. The RH value was ensured maintained at the required value for at least 24 h before the testing was conducted.

The procedures are as follows:

(1) Samples (m ≈ 1 g) were prepared by oven heating at $T = 110°C$ for $t = 24$ h and then allowed to cool to room temperature in a desiccator for $t = 1$ h prior to testing.
(2) The samples were placed in the hanging dish suspended below the balance and $\Delta m = m_w - m_{dry}$ (g) monitored continually using a load cell for every second.
(3) For this test, dynamic vapor sorption (DVS) of each material $(\Delta m/m_{dry})\% = (m_w - m_{dry})/m_{dry}$ were compared when the materials was placed in the chamber until the mass

difference between the successive mass change is quasi constant or when the consecutive change in mass $< \pm 5\%$ The results for the time taken to reach equilibrium state with RHie and the change in mass are summarized in the following Table 5.

The results are analyzed for each of the materials. It is important to note that, in characterizing the hygrothermal properties of the materials, other than overall moisture uptake, the rate of that uptake or the sorption kinetics is also important, of which as claimed in Ref. [2], sometimes the rate of the sorption uptake is even more important and a rapid response to the change in the relative humidity of the environment is important in producing the required thermal reaction.

With vermiculite mixed with LiCl-CaCl$_2$ in comparison to vermiculite impregnated with single salt of CalC$_2$, the key finding of the characterization analysis is that when mixed with LiCl which has lower DRH value, the time taken for the materials to reach equilibrium state is significantly shorter for both low RHie values (i.e. 17% and 40%) and high RHie values (i.e. 75–92%). This is due to the sorption kinetics that is significantly improved which is very important for effective discharging/charging cycles and high rate of heat extraction as the rate of heat generation is directly related with the sorption kinetics.

The amount of the sorption uptake is also on average higher compared to vermiculite with CaCl$_2$ with the measurement at RHie value within 40% displays overall moisture uptake higher by 36%. Meanwhile, for vermiculite-MgSO$_4$ when mixed with MgCl$_2$ at low RH values (i.e. 17% and 40%), there's is an undetectable changes in the mass of the materials, and thus we can conclude that the performance of the salts mixtures at low RHie values are not promising. However, at RHie values of 75%, the time taken for the materials to reach its equilibrium state is shorter in comparison to vermiculite with MgSO$_4$. Meanwhile, the change in the amount of the overall moisture uptake is as high as 1.66 (kg/kg) which is almost 2% higher than Vermiculite with MgSO$_4$ only.
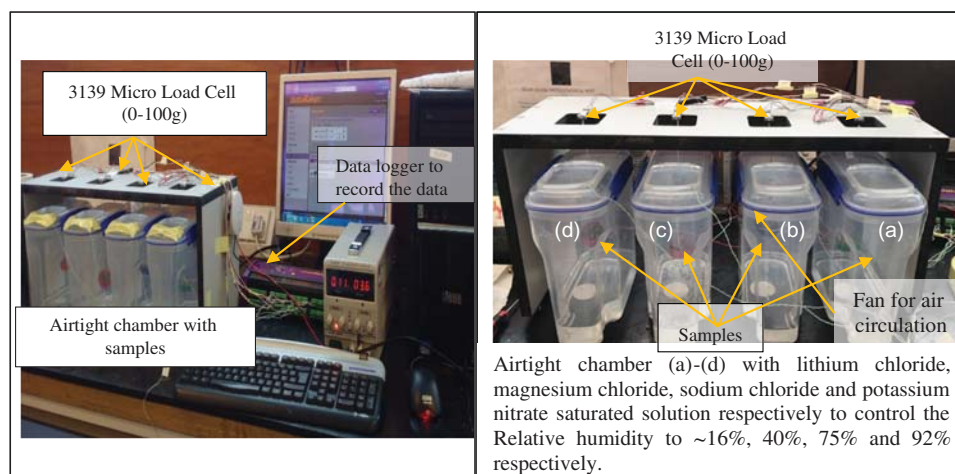

Figure 7. A custom built successive desiccator chamber system.

Table 5. *Sorption isotherm analysis which shows time taken to reach equilibrium (t_{eq}) and the change in the mass of the sorption materials.*

	RHie 17%		RHie 40%		RHie 75%		RHie 92%	
	t_{eq}(h)	Δm (kg/kg)	t_{eq}(h)	Δm (kg/kg)	t_{eq}(h)	Δm (kg/kg)	t_{eq}(h)	Δm (kg/kg)
Vermiculite with LiCl-CaCl$_2$	15.90	0.14	12	1.99	73.29	1.90	69.00	2.78
Vermiculite with MgSO$_4$-MgCl$_2$	N/A	N/A	N/A	N/A	44.50	1.16	68.85	2.01
Vermiculite with MgSO$_4$-CaCl$_2$	52.45	0.17	4.75	0.26	42.93	0.38	157.33	0.93
Vermiculite with CaCl$_2$ [2]	93.25	1.19	118.45	1.46	145.68	1.46	153.69	1.58
Vermiculite with MgSO$_4$ [2]	4.32	0.02	5.76	0.06	62.06	0.41	68.64	0.68
Silica gel with KCOOH	N/A	N/A	43.00	0.20	33.00	0.56	40.00	0.71

Another important finding that worth discussing is the performance of the Vermiculite with MgSO$_4$-CaCl$_2$. Earlier, we have mentioned that Vermiculite with MgSO$_4$ has a high energy density. However, the material does not show a significant change in mass increase at low RHie value. Hence, the performance of the material may be further optimized by mixing MgSO$_4$ with salt solution that have lower DRH value. Thus, vermiculite was impregnated with MgSO$_4$-CaCl$_2$. Unlike Vermiculite with MgSO$_4$-MgCl$_2$ and Vermiculite with MgSO$_4$, when mixed with CaCl$_2$, the thermochemical reaction which occurs at RHie value about 40% is noticeable with average sorption uptake of 0.26 kg/kg and the time taken for the sorption process to reach equilibrium is shorter when compared to vermiculite with CaCl$_2$ only, and vermiculite with MgSO$_4$ only. Although, the amount of the sorption uptake is not as high as vermiculite with CaCl$_2$. The composite THS materials, have the highest energy density which is almost 40% higher in comparison to vermiculite with MgSO$_4$ which may imply high temperature lift within the given reaction time. In the current research, the performance of the THS materials is limited to the mixing ratio of both salts at 50% ratio. With this being said, the potential of the composite materials with vermiculite mixed MgSO$_4$-CaCl$_2$ may be further optimized with different salts mixed ratio. For KCOOH impregnated into silica gel, the sorption performance was also investigated. In general, the composite materials requires 40 h to reach equilibrium with the highest amount of the overall moisture uptake of 71 kg/kg at RHie 92%. At RHie 75% the amount of the sorption uptake may be considered as high as 0.56 kg/kg with the rate of the sorption uptake of only approximately 33 h.

6 CONCLUSIONS

Innovative nano-composite materials using MgCl$_2$-MgSO$_4$, CaCl$_2$-LiCl and MgSO$_4$-CaCl$_2$ salts mixtures impregnated into vermiculite, and the use of cheap, non-corrosive and environmentally friendly KCOOH impregnated into silica gel have been proposed and discussed. The samples were prepared and material characterization analysis was conducted. Most conventional matrices such as zeolites and silica have high regeneration temperatures that make the use of these materials in THS very challenging. The new salt composites may be a promising option for developing

THS systems charged via solar thermal systems. According to the results of the study, the following conclusions could be drawn:

The energy density analysis suggests that the vermiculite with salts mixture is a promising candidate for a THS system compared to composite material with individual salts. The energy densities of the composite materials or SIM with salts mixtures are in general 200 kJ/kg higher than the composite materials with individual salts. Meanwhile, a significant increase in energy density is demonstrated by THS materials using vermiculite-MgSO$_4$-CaCl$_2$ such that energy density as high as 1752.4 kJ/kg is given from the DSC analysis.

Higher mass loss obtained from the TGA analysis indicating that the sorption heat of the salt hydrates was enhanced as a result of the salts mixtures. From all the THS materials being investigated, vermiculite-MgSO$_4$-CaCl$_2$ has demonstrated the highest amount of mass loss within a given temperature range.

Despite its high energy density and the high mass loss displayed from the TGA analysis, the overall moisture sorption uptake of vermiculite-MgSO$_4$-CaCl$_2$ at low internal relative humidity of the chamber, (i.e. RHie 17% and RHie 45%), mid-range value (i.e. RHie 75%) and high value (i.e RHie 92%), are not as significant as Vermiculite with LiCl-CaCl$_2$ or vermiculite with CaCl$_2$. Nevertheless vermiculite-MgSO$_4$-CaCl$_2$ has displayed lowest rate of sorption uptake at RHie 40% and RHie 75% in comparison to Vermiculite with LiCl-CaCl$_2$, vermiculite with CaCl$_2$ and vermiculite with MgSO$_4$.

Due to the advantages of KCOOH over typical salts, the potential of KCOOH impregnated into silica gel as THS materials was explored. However, the DSC analysis has shown that KCOOH-silica gel has energy density as low as 457 kJ/kg which may be considered low in value in comparison to other THS materials being investigated. In addition, the TGA analysis has shown that the amount of mass loss which represents the regeneration of the composite KCOOH-silica gel is only approximately 5% within 30–140°C of heating temperature.

7 FUTURE WORK

This paper discusses thermochemical materials suitable for short-term and long-term heat storage for building application. In addition, the THS system aimed to be powered by solar energy or waste heat during material regeneration. Thus, in addition to high energy density, the materials must be able to

regenerate at temperature within 60–80°C. From the initial screening, we may conclude that innovative material using vermiculite impregnated with the salts mixtures of $MgSO_4$-$CaCl_2$ as a promising material. Nevertheless, the materials can be further optimized by modifying the salts mixing ratio in reaching the balance between the enthalpy capacity and the hydration rate (discharging rate) process of the thermochemical materials.

This research serves as a preliminary investigation on combination of salts mixtures in vermiculite host matrix. The scope of the research is limited to a single mixing ratio of salts. Future research could investigate different mixing ratios for the investigated composites especially for $MgSO_4$ with $CaCl_2$. Due to the low DRH value of $CaCl_2$, the increase in the ratio of $CaCl_2$ in the mixture of $MgSO_4$ with $CaCl_2$ is believed to improve the amount of the overall moisture uptake and the rate of the sorption uptake. Combinations of other potential candidate salts, including $LiNO_3$, LiBr, SrBr, $CaNO_3$, could be investigated. Meanwhile, the potential of KCOOH as THS materials will be further explored by impregnating the material in porous host matrixes such as activated carbon, metal organic frameworks, activated alumina, graphite, silica gel or zeolite is another potential research direction.

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