

Vermiculite/LiCl Composite for Adsorption Thermal Energy Storage

Suboohi Shervani, Curtis Strong, F. Handan Tezel*

Department of Chemical and Biological Engineering, University of Ottawa
161 Louis-Pasteur, Ottawa, Ontario K1N 6N5, Canada
sshervan@uottawa.ca; cstro043@uottawa.ca; handan.tezel@uottawa.ca

Abstract – Sorption based thermal energy storage systems are amassing more attention of the researchers, due to their high energy storage density, stability and cyclic performance. Several materials have been used for adsorption based thermal energy storage technology. One promising group of materials are hygroscopic salts (e.g. metal chlorides), due to their high energy storage density and water vapour sorption capacity. However, hygroscopic salts are difficult to handle due to deliquescence and issues of cyclic stability. One method of stabilizing hygroscopic salts is to impregnate a host material with them to form a salt-in-matrix composite. Vermiculite is considered to be a good candidate as a host material for salt-in-matrix composites for thermal energy storage due to its high porosity, high stability, and low cost. Pure vermiculite has low energy storage density in comparison to traditional adsorbents. However, when vermiculite is impregnated with LiCl energy storage density values of up to 159 kWh/m³ can be achieved at 50% relative humidity after a regeneration temperature of 120°C. This paper includes the synthesis and characterization, e.g. structural and thermal energy storage properties of the vermiculite based composite.

Keywords: Vermiculite, Thermal Energy Storage, Adsorption, Space Heating, Energy Storage Density

1. Introduction

Climate change has become a most concerning issue in the world due to the use of fossil fuels in our day-to-day life [1]. The use of fossil fuels generates carbon dioxide emission and results in global warming. The use of renewable energy can be a good way to combat this serious issue. Solar thermal energy is a good alternative to thermal energy produced from fossil fuels. However, due to the inconsistent output of solar thermal energy, the energy that is produced cannot be fully utilized. So, thermal energy storage systems have emerged as a promising technology to utilize the solar thermal energy to the fullest extent [2, 3]. Adsorption thermal energy storage is gathering more attention among the researchers as it exhibits high energy storage density, durability and can be used for long term energy storage applications [4]. Several types of adsorbents have been used for adsorption thermal energy storage [5, 6]. Hygroscopic salts are one promising candidate for thermal energy storage, due to their high energy storage density and water uptake. However, these materials can become deliquescent, making them difficult to handle and resulting in low cyclic stability. One method of stabilizing hygroscopic salts is to impregnate them into a matrix, forming a salt-in-matrix composite. Vermiculite is a good recyclable mineral and can be used for thermal energy storage application due to its high porosity [7]. The high porosity of vermiculite makes it possible to be impregnated with large quantities of salts. Vermiculite has also been used as a matrix material to contain phase change materials for phase change-based thermal energy storage. Song et al. modified the expanded vermiculite (EVM) by acid leaching with different concentrations (0.01, 0.05, and 0.1 mol/L) of HCl solution to improve its properties as a matrix material to contain polyethylene glycol (PEG), a popular material for phase change-based thermal energy storage [8]. The thermal conductivity of the vermiculite/PEG composite was 0.43 W/mK, and the latent heat of 144.7 J/g was achieved. Deng et al. also used vermiculite as an encapsulating material for phase change based thermal energy storage [9]. They prepared LiNO₃, NaNO₃, and KNO₃ based vermiculite composites by impregnation and separation method. Their tests indicated that the phase change temperatures of three composites were between 243.1 and 325.1°C and that latent heats were between 83.1 and 295.4 J/g. The thermal conductivity of LiNO₃, NaNO₃ and KNO₃ based vermiculite were 0.51, 0.44, and 0.33 W/(m K), respectively, indicating acceptable thermal energy charging/discharging rates. Zhang et al. synthesized the vermiculite/LiCl composite by impregnation method [10]. For this composite, the water uptake was 1.41 g/g, the mass energy storage density was 1.21 kWh/kg, and the volumetric energy storage density was 171.61 kWh/m³. Zhang et al. prepared a SrBr₂ based vermiculite composite for low temperature thermal energy storage [11]. The composite showed water uptake of 0.53 g/g, mass energy storage density of 0.46 kWh/kg and volumetric energy storage density of 105.36 kWh/m³. Brancato

et al. prepared a vermiculite and inorganic salt based composite by a dry impregnation method for thermal energy storage [12]. Their results demonstrated slower interaction kinetics in the vermiculite-based composites, due to the larger size of salt grains embedded in the pores, while promising volumetric energy storage density of 194.44 kWh/m³ was observed.

The current paper describes the synthesis, and thermal energy storage properties of a vermiculite/LiCl composite. The composites were tested in an open thermal energy storage system with breakthrough experiments. The temperature and concentration breakthrough curves are also presented.

2. Materials and Method

Vermiculite/LiCl composite was prepared by impregnating vermiculite with LiCl. Vermiculite was purchased from Sigma Aldrich (Toronto, Canada) and LiCl was purchased from Thermo-fisher Scientific (Toronto, Canada).

2.1. Synthesis of Vermiculite/LiCl Composite

The synthesis procedure was the same as used by Shervani et al. [3]. 10 g of Vermiculite, 10 g LiCl, 5 ml ethanol and 100 ml of deionized (DI) water were mixed in a glass beaker and the solution was stirred for 24 hours at room temperature. Afterwards, the composite was set for drying for 48 hours at 70°C.

2.2. Thermal Energy Storage Characteristics

The thermal energy storage characteristics were measured using the lab-scale thermal energy storage setup shown in Figure 1 [13]. The building air was split into two streams: wet and dry. The dry air stream went to the mixing chamber through a desiccant column. Wet air stream passed through a humidification chamber which was attached to a water tank that gets filled automatically by a positive displacement pump when the water level in the humidification chamber decreases. The wet air stream then went into the mixing chamber where it was mixed with the dry air stream. The ratio of the flowrates of these two streams was adjusted using a PID controller to attain the desired relative humidity at the inlet of the column during the hydration. In this study, 50 % relative humidity was used at the inlet. Electric heater was used for heating the adsorption column to 120°C for its regeneration before starting the humidification experiments, as well as regenerating it between different cycles. After the regeneration of the adsorption column at 120°C, it was cooled down to room temperature before the air at 50 % relative humidity entered the adsorption column for the humidification experiments. There are three valves attached to the system; 1. Solenoid valve, which controls the inlet stream flow to the bypass or to the column, 2. System valve, which allows/prohibits the air into the column, 3. Check valve, which is a one-way valve to avoid the back flow of ambient moist air into the column. Two mass flow controllers were also attached to the system, to control the flow-rates of the dry and wet air streams. Several pressure indicators, thermocouple and humidity indicators were attached to the system for us to obtain the concentration and the temperature breakthrough curves during the hydration experiments.

The energy storage density value was calculated by first determining the heat released during the hydration experiments from Equation (1) as follows:

where, m_{air} is the mass flow rate of air (g/min), $C_{p,air}$ is the heat capacity of air (kJ/g °C), T_{in} is the inlet temperature

$$Q_{hydration} = \int_0^t m_{air} C_{p,air} (T_{out} - T_{in}) dt \quad (1)$$

(°C), and T_{out} is the outlet temperature (°C). Based on $Q_{hydration}$, the energy storage density (ESD) can be calculated by dividing $Q_{hydration}$ by the column volume (7.09 cm³) [14].

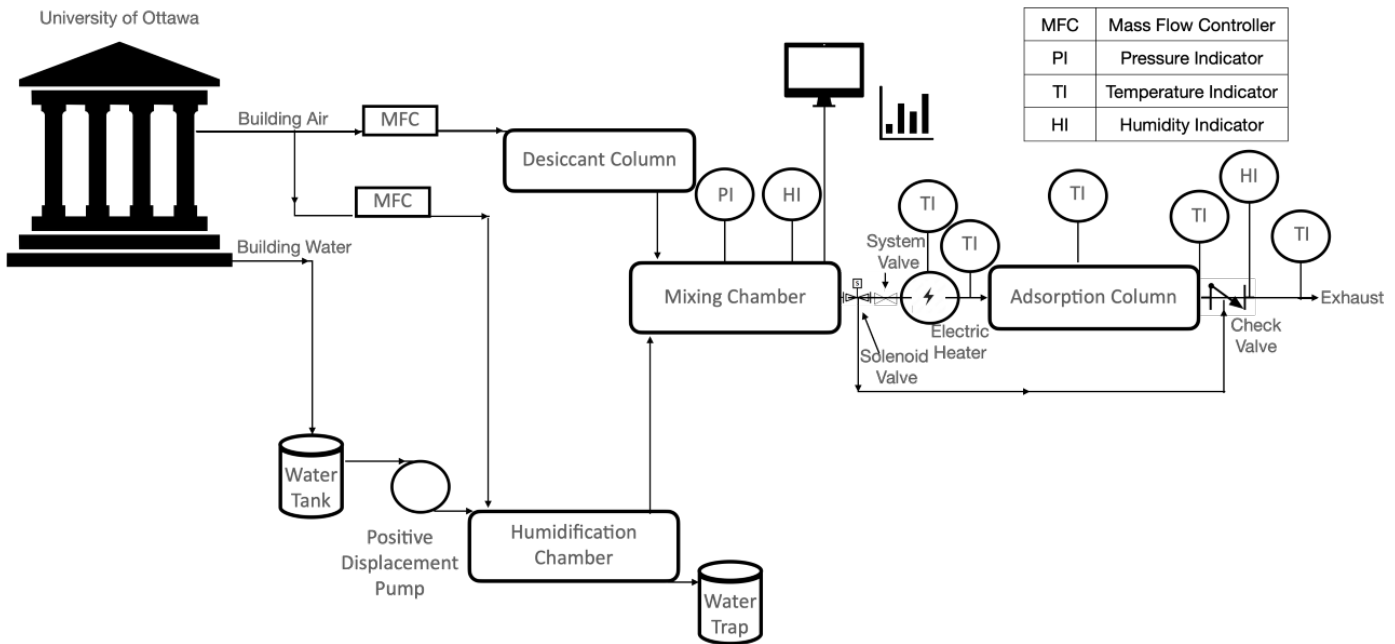


Figure 1: Schematic diagram of lab-scale thermal energy storage setup.

3. Results and Discussions

The energy storage density (ESD) of vermiculite/ LiCl composite was tested using a lab scale energy storage set-up. Silica gel has been taken as standard material for the comparison of the energy storage properties of the pure vermiculite, and vermiculite/LiCl composite. The energy storage density of silica gel was mentioned by Strong et al. [14]. Figure 2 shows that pure vermiculite has very low energy storage density of 5 kWh/m^3 at 50% RH at the inlet after regeneration at 120°C . Silica gel is showing 114 kWh/m^3 energy storage density with good stability for the three cycles, whereas vermiculite/LiCl composite is showing a higher energy storage density of 159 kWh/m^3 at 50% RH at the inlet after regeneration at 120°C for the first cycle. But, for the second and third cycles, the ESD of the vermiculite/LiCl composite drops steadily. This is because LiCl has a low deliquescence relative humidity which is causing it to liquify and exit the pores of the host matrix. Therefore, it is to be noted that salt hydrates with higher deliquescence relative humidities may be better suited for this type of application. Another option would be to encapsulate the composite with an encapsulating agent [4]. It is suggested that encapsulating the vermiculite/LiCl composite with an encapsulating agent will solve the stability issue, which could make vermiculite/LiCl composite more promising for thermal energy storage applications.

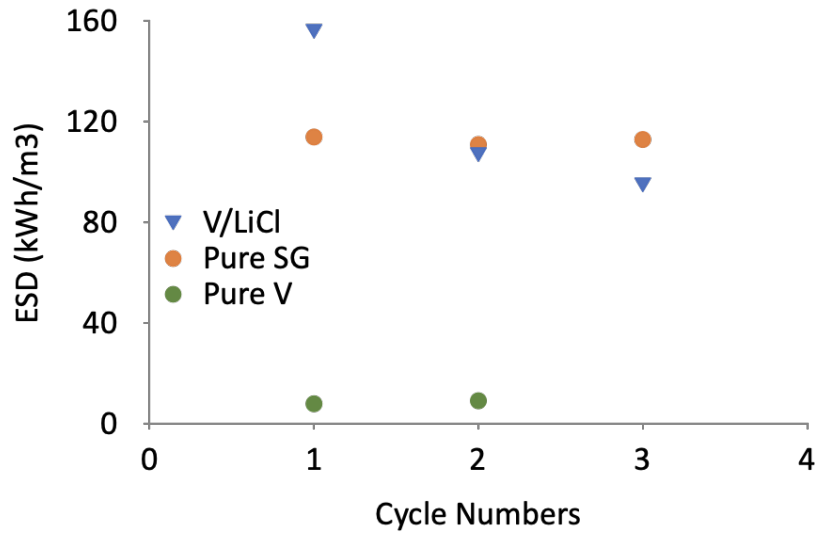


Figure 2: Comparison of ESDs of vermiculite/LiCl composite with silica gel and pure vermiculite at 50 % RH at the inlet after regeneration at 120°C.

Figure 3 (a) shows the concentration breakthrough curves of three consecutive cycles of vermiculite/LiCl composite. All three cycles have shown the same trend which shows that the concentration profile in all three cycles have remained the same. Figure 3 (b) shows the temperature breakthrough curves which shows the temperature lifts between 3 and 4°C, and the profiles remain similar, however for the first cycle, more temperature difference was observed than the rest of the two cycles, which caused the decrease in ESD for consecutive cycles.

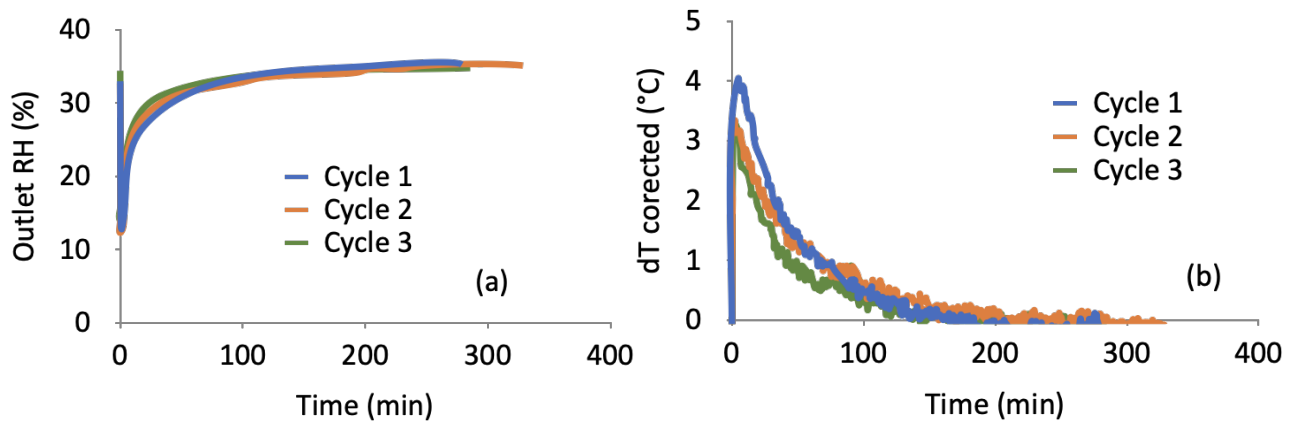


Figure 3: (a) Concentration, and (b) Temperature breakthrough curves of vermiculite/LiCl composite at 50 % RH at the inlet after regeneration at 120°C. dT indicates the temperature difference between the inlet and the outlet of the column.

4. Conclusion

In this study, a vermiculite/LiCl composite was synthesized by impregnation method. The thermal energy storage characteristics were measured using a lab scale thermal energy storage setup. The composite exhibited high energy storage density (159 kWh/m³) at 50%RH at the inlet after regeneration at 120°C. This is more than silica gel, a commercial desiccant which has been studied extensively for thermal energy storage applications. However, the vermiculite/LiCl composite

showed stability issues, which can be overcome either by encapsulating the composite by an encapsulating agent or using a salt with a higher deliquescence relative humidity. MgSO_4 is a good option and possesses high deliquescence relative humidity (92% at 25°C) [2]. However, since MgSO_4 has lower theoretical energy storage density than LiCl [15] the best option would be to encapsulate the composite with an encapsulating agent.

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