

The effects of graphite flake on specific cooling power of sorption chillers: An experimental study

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Abstract

Adding natural graphite flakes to sorbents of sorption cooling systems can enhance the total thermal diffusivity, while reducing the active material and increasing mass transfer resistance. To find the best compromise between these counteracting trends, the specific cooling power (SCP) of CaCl₂-silica gel composite sorbents with 0-20 wt% graphite flake content was tested with a custom-built gravimetric large pressure jump (G-LPJ) test bed. It was observed that when the sorption rate is high, i.e. the first 20 min of sorption, graphite flake additive increases the SCP and COP due to the higher sorbent thermal diffusivity. Nevertheless, as the sorption rate reduces with time, the need for heat transfer enhancement, i.e. graphite flake additive, decreases. Furthermore, adding 20 wt.% graphite flakes to the composite sorbent has led to a 67% increase in SCP_{0.8}.

Keywords: Sorption cooling system, graphite flakes, heat transfer enhancement, specific cooling power, thermal diffusivity

Introduction/Background

Vapor compression refrigeration systems consume approximately 15% of global electrical energy and use environmentally harmful refrigerants [1]–[3]. Due to climate change and economic development, cooling demand is expected to increase [4]. Sorption cooling systems are an alternative clean technology in which an environmentally friendly refrigerant, such as water, is adsorbed by a sorbent material. Sorption cooling systems that utilize materials with low regeneration temperatures can be powered by low-grade heat sources (temperature sources around 80 °C), including solar thermal energy and industrial waste heat [5]. However, commercialization of sorption cooling systems is limited by fundamental challenges, including low specific cooling power (SCP) due to poor heat transfer between sorber bed heat exchanger (HEX) and the sorbent [6]–[8]. Sorber beds need to be cooled during the sorption process and heated during the desorption process. This oscillatory cooling and heating is performed with a heat transfer fluid flowing through the sorber bed HEX. As such, heat transfer characteristics of the sorbent and HEX are crucially important to the overall performance and SCP of the sorption systems. It was shown in our previous study [9] that the sorbent thermal diffusivity is the main limiting factor in the heat transfer from the sorbent to the heat transfer fluid through the heat exchanger.

Thermally conductive materials can be added to the sorbent to enhance the thermal diffusivity of the adsorbent bed [10], [11]. The addition of high thermal diffusivity material can form higher conductivity paths by filling up the pores in the microstructure of the adsorbent particles to increase the overall thermal diffusivity. However, in general, these additives decrease the active material fraction and increase the vapor transport resistance [12]. Moreover, many microporous adsorbents have open pore structures and high total pore volumes [13]; as a result, significant improvements in thermal diffusivity of microporous adsorbent materials have been limited to high additive fractions (>10 wt%), compromising the total adsorption capacity.

Graphite is by far the most selected additive when developing composite sorbents with the purpose of enhancing thermal conductivity [14]. When comparing different host matrices or/and additives, graphite presents the highest conductivity values [15]. For instance, Mauran et al. [16] reported thermal conductivities of about $10\text{-}40 \text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$ for CaCl_2 -expanded natural graphite (ENG). Nonetheless, high concentrations of ENG are used and in some cases the sorbent is compressed to enhance thermal conductivity, which considerably reduces the sorption capacity.

Guilleminot et al. [17] reported that thermal conductivity of the expanded graphite/zeolite composite can be increased up to $10 \text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$ compared to $0.09 \text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$ for the packed bed of same adsorbent. However, they did not report the sorption capacity. Pino et al. [13] found that by increasing the graphite content in 4A-zeolite-based composites, the equivalent thermal conductivity increases and the equilibrium uptake decreases. Wang et al. [18] found that by adding expanded graphite to CaCl_2 consolidating the composite, the thermal conductivity was enhanced up to $9.2 \text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$. The uptake was not reported in their study.

Eun et al. [19] found that adding expanded graphite to silica gel, increases the thermal conductivity of the composite sorbent. They also observed that by increasing the graphite content, the water uptake increases because of the enhanced thermal conductivity. However, the graphite weight, which acts as dead weight, was not included in their calculations.

Zheng et al. [20] fabricated composite sorbents by combining silica gel with expanded natural graphite treated with sulfuric acid (ENG-TSA) as the host matrix. It was found that by increasing the graphite content, thermal conductivity, thermal diffusivity and water uptake increase. Nonetheless, their water uptake calculation did not include the graphite mass.

Fayazmanesh et al. [21] combined calcium chloride in a silica gel matrix with a binder and graphite flakes to produce water absorbent consolidated composites. The addition of 20 wt.% graphite flakes increased the thermal conductivity of the composite adsorbent from 0.57 to $0.78 \text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$. The equilibrium uptake of samples at a 1.2 kPa vapor pressure decreased from 0.32 g/g for CaCl_2 /silica gel to 0.15 g/g for silica gel/ CaCl_2 consolidated with 10 wt.% graphite flakes and 13 wt.% binder.

It is evident from the literature that the majority of the studies only reported the effect of additives on the equilibrium uptake. However, due to the transient behavior of adsorber beds, the sorbent does not become fully saturated/dried during sorption/desorption in sorption cooling systems. The studies that investigated the transient behaviour of the uptake, reported the sorption capacity per mass of “active material”, while the additive mass, as part of the composite sorbent, should be included in the calculations of water uptake. In this paper, CaCl_2 -silica gel composite sorbents with 0-20 wt% graphite flake contents are prepared and tested in a custom-built gravimetric large pressure jump (G-LPJ) test bed to study the counteracting effect of graphite additive on the transient heat and mass transfer performance and SCP of sorption cooling systems.

Sample preparation

Polyvinylpyrrolidone (PVP40) binder (40,000 MW, Amresco Inc.) was dissolved in water; subsequently, CaCl_2 and silica gel (SiliaFlash[®] B150, Silicycle, Inc., Quebec, Canada) and graphite flakes (consisting of both $150 \mu\text{m}$ fine particles and thin flakes up to 1.3 mm long, Sigma-Aldrich) were added to the aqueous solution. The composition and total mass of the sorbent composites prepared in this study are presented in Table 1. Sorbent mass was measured using an analytical balance (OHAUS AX124) with the accuracy of 0.0001 g and sorbent thickness was measured using a digital caliper (Mastercraft 58-6800-4) with the accuracy of 0.01 mm.

Thermal diffusivity of composite sorbents was measured with a transient plane source, hot disk thermal constants analyzer, as per ISO 22007-2 [22] (TPS 2500S, ThermTest Inc., Fredericton, Canada) for different graphite flake contents and presented in Table 1.

Table 1. Compositions, total mass, and measured thermal diffusivity of the sorbent composite samples

No.	Silica gel (wt.%)	CaCl ₂ (wt.%)	PVP40 (wt.%)	Graphite flake (wt.%)	Mass (g)	Thickness (mm)	Thermal diffusivity (m ² /s)
1	45.0	45.0	10	0	18.8068	5.15	0.23e-6
2	42.5	42.5	10	5	18.7018	5.12	0.34e-6
3	40.0	40.0	10	10	18.7841	5.08	0.41e-6
4	37.5	37.5	10	15	18.6930	5.09	0.98e-6
5	35.0	35.0	10	20	18.8815	5.06	1.38e-6

The solution of composite sorbent was coated on graphite sheets and oven dried at 70 °C and then 180 °C, each for 1 h. The composite sorbent with 20 wt% graphite flake content is shown in Fig. 1.

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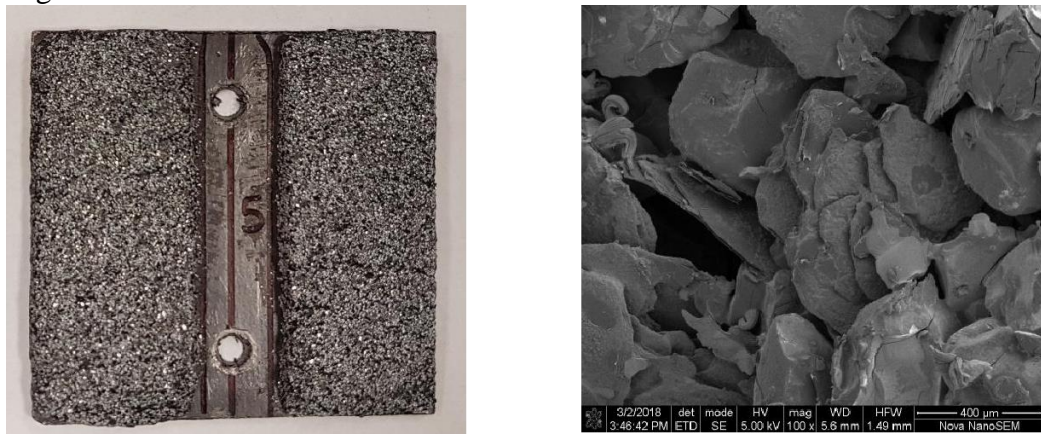


Fig. 1. The composite sorbent with 20 wt% graphite flake content coated on graphite sheets (left), SEM image (right)

Experimental test-bed and measurements

A new gravimetric large pressure jump (G-LPJ) test bed was custom-built in our lab to investigate the heat and mass transfer performance of sorbent materials. The coated sorbent samples were bolted to a copper heat exchanger, see Fig. 2.



Fig. 2. Sorbent composite bolted to copper heat exchanger

A schematic diagram and a picture of the G-LPJ test bed is shown in Fig. 3. Heat transfer fluid flows through the copper heat exchanger and maintains its temperature constant at 39 °C. The sorber bed and the copper heat exchanger are placed inside a vacuum chamber which is connected to a capillary-assisted evaporator whose temperature is changed between 1 °C and 20 °C for desorption and adsorption, respectively. The whole test bed is vacuumed for 6 hours using a vacuum pump to dry the sorbent material. The vacuum chamber is placed on a precision balance (ML4002E, Mettler Toledo) with an accuracy of 0.01 g to measure the mass of the sorbate uptake. K-type thermocouples with an accuracy of 1.1 °C are passed via a feed-through in the vacuum chamber to measure the sorbent temperature. The pressure of the sorber bed and the evaporator is measured using 722B Baratron pressure transducer with the accuracy of 0.5%. The instruments are interfaced with a PC through a data acquisition system and software built in the LabVIEW environment.

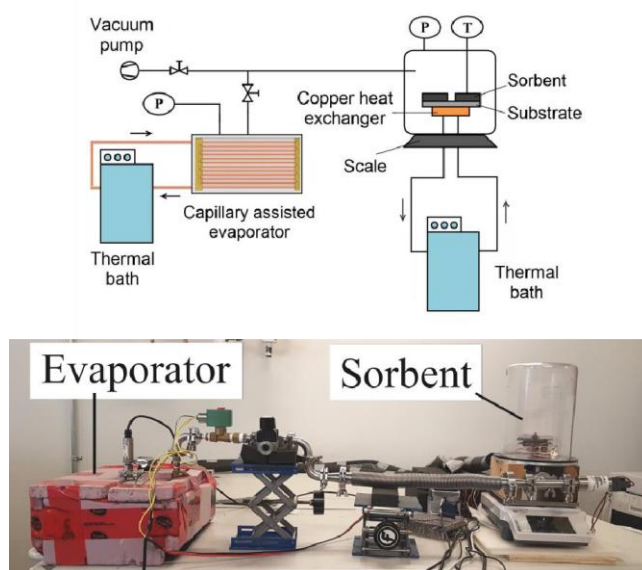


Fig. 3. Schematic (top) and picture (bottom) of the gravimetric large pressure jump test-bed

Discussion and Results

Fig. 4 shows that the sorbent temperature decreases more rapidly for samples with greater graphite flake content. One reason is that by adding graphite flake, the sorbent thermal diffusivity increases, which enhances the heat transfer from the sorbent to the HEX, see Table 1.

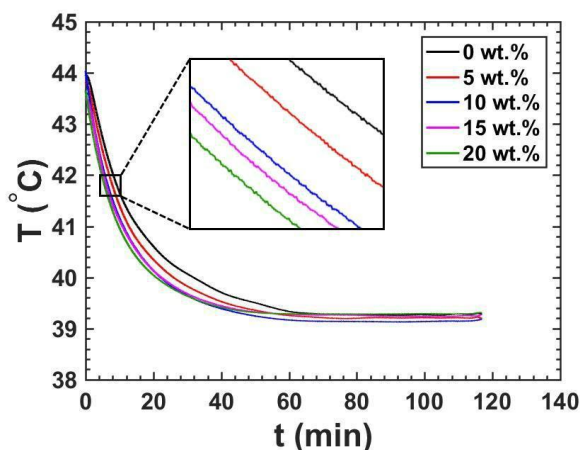


Fig. 4. Variation of sorbent temperature data collected in our G-LPJ testbed versus time for various graphite flake contents

Furthermore, the heat generation decreases for samples with larger graphite flake content as they have less active material.

The isotherm of the sorbent material was obtained using an IGA-002 thermogravimetric sorption analyzer (TGA) (Hiden Isochema). Sorbent material was placed on the sample cell, which is held by a microbalance to measure the mass changes of the sorbent, while the temperature and pressure are controlled. The mass changes of the sorbent are collected in the range of 0.04–2.84 kPa (our range for G-LPJ) with the pressure step of 0.2 kPa at 25°C. More details regarding the TGA measurements can be found elsewhere [21].

Fig. 5 shows the variation of water uptake with time for various graphite flake contents. As shown in Fig. 5, the equilibrium uptakes measured with the G-LPJ test bed are in good agreement with TGA equilibrium data. Moreover, as can be seen for the region that sorption rate ($d\omega/dt$) is high, i.e. the first 20 min, the water uptake increases by increasing the graphite flake content, as expected. The reason is that during this time, the heat generation rate in the sorbent is high; hence, there is a high need for enhanced sorbent thermal diffusivity; thus, increasing the graphite flake enhances the overall performance. However, as the sorbent approach saturation, the trend starts to reverse, which means that the uptake increases with a decrease of graphite content. That is because as the sorbent approaches equilibrium, the heat generation rate reduces; as a result, the need for enhanced heat transfer decreases; consequently, the sorbent with higher active material can uptake more which leads to higher performance.

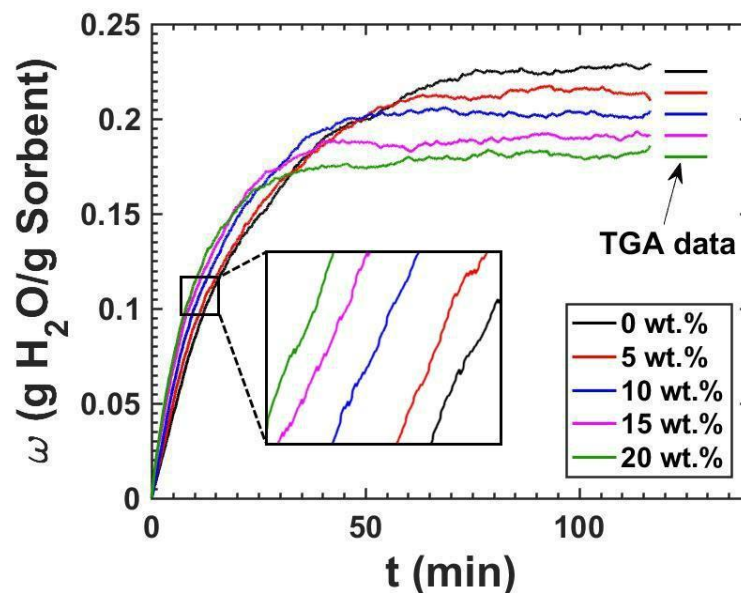


Fig. 5. Variation of water uptake data collected in our G-LPJ testbed versus time for various graphite flake content composites

Specific cooling power (SCP) is defined as the ratio of cooling energy to the product of sorbent mass and cycle time which represents the performance of sorber beds, as shown in Eq. (1).

$$SCP = \frac{Q_{evap}}{m_{sorb}\tau} = \frac{\Delta\omega h_{fg@T_{evap}}}{\tau} \quad (1)$$

ω	Water uptake (g/g)
h_{fg}	Evaporation enthalpy (J/kg)
τ	Cycle time (s)

Fig. 6. shows the experimental SCP data collected in our G-LPJ testbed for various sorption times and different graphite flake contents. It can be seen that adding graphite flake enhances the SCP because the sorbent thermal diffusivity increases. Furthermore, it can be observed that by reducing the sorption time, the SCP enhancement of adding graphite flake, increases because the heat generation rate increases. In addition, it is shown that adding 15 wt.% graphite flake or more, results in a significant increase in SCP for short sorption times. The reason can be attributed to the better connection between graphite flakes that can be established for composites with more than 10 wt.% additives.

A practical specific cooling power was proposed by Aristov et al. [23] to be calculated when the uptake reaches 80% of the equilibrium. Fig. 7 shows the effect of graphite flake on SCP0.8. It can be observed that SCP0.8 increases with the increase of graphite flake content because the heat transfer rate increases; thereby reducing the time required for the sorbent to reach equilibrium. For example, composite sorbent containing 20 wt.% graphite flake has a 67% greater SCP0.8 than the composite sorbent with no thermally conductive additive.

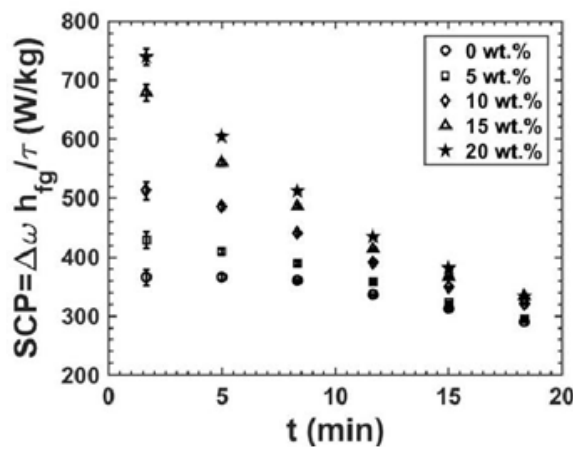


Fig. 6. Variation of specific cooling power versus sorption time for various graphite flake contents

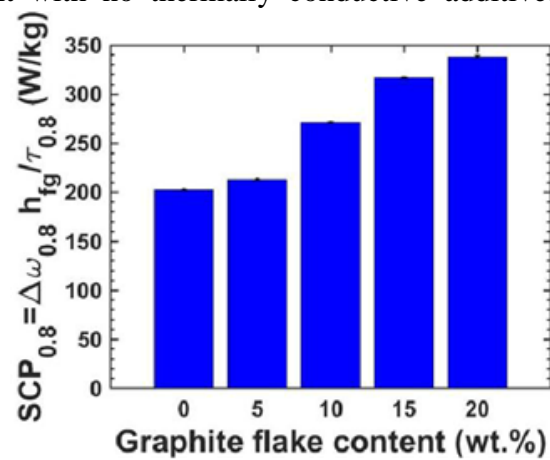


Fig. 7. Variation of SCP0.8 versus graphite flake contents

Coefficient of performance (COP) is defined as the ratio of evaporative cooling energy to the input energy (Eq. (2)). Fig. 8 shows the variation of COP with time for different graphite flake contents. It can be seen that COP increases by increasing the graphite flake content as the sorbent thermal diffusivity and sorbate uptake increase; thus, evaporative cooling energy increases.

$$COP = \frac{Q_{evap}}{Q_{input}} = \frac{m_{sorb} \int_{ads} \frac{d\omega}{dt} h_{fg} dt}{\int_{des} \left(\left(m_{sorb} (c_{p,s} + \omega c_{p,w}) + m_{HEX} c_{p,HEX} \right) \frac{dT}{dt} - m_{sorb} \frac{d\omega}{dt} h_{ads} \right) dt} \quad (2)$$

c_p	Specific heat capacity (J/kg K)	T	Temperature (K)	t	Time (s)	
Subscripts	s, sorb	Sorbent	w	Water	HEX	Heat exchanger

Summary/Conclusions

The effect of adding graphite flakes on the SCP and COP of sorption cooling systems was studied using a custom-built G-LPJ testbed. It was found that for high sorption rates, the sorber bed performance enhances by adding graphite flake due to the higher sorbent thermal diffusivity; however, as the sorbent approaches equilibrium, the performance deteriorates by adding graphite flake because of the less active material. Therefore, there exists an optimum

graphite flake content to achieve the highest SCP and COP, which will be investigated in our future study.

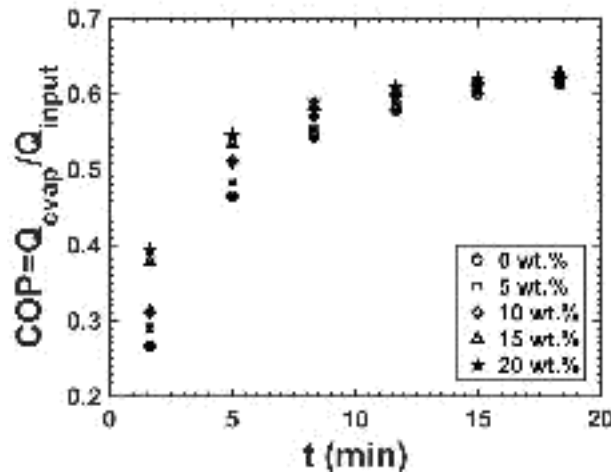


Fig. 8. Variation of COP versus sorption time for various graphite flake contents

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