Effect of Conductive Additives on Performance of CaCl₂-Silica Gel Sorbent Materials

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Abstract

Several CaCl₂-silica gel composite samples were prepared with a range of added carbon nanotubes (CNT) and graphite flakes (GF). Water uptake, thermal conductivity, and thermal diffusivity of the samples were tested to establish an optimum composition for the consolidated composites. Results indicate that: i) GF and CNTs have various structural effects and different optimum loadings to improve the performance of the composites, ii) thermal conductivity and diffusivity of the composites increases up to 376% and 483% by addition of conductive additives; iii) thermal property improvement associated with CNT addition is limited due to possible agglomeration of CNTs within a specific binder volume in the composite matrix while the increase in thermal properties with GF shows linear relationship; iv) water uptake reduces by increasing additives. The results show potential for optimization of sorption composite using conductive additives for various applications ranging from thermal storage to chillers.

Keywords: Sorbent material, Adsorption, Silica gel, Graphite flakes, Carbon nanotube

Introduction

Adsorption cooling systems (ACS), in which low-grade waste heat or renewable energy sources are used, are environmentally benign systems that are being considered as viable alternatives to compression refrigeration systems [1-5]. However, there are significant challenges and operational complexities facing widespread application of ACS including low specific cooling power (SCP) and relatively large specific mass and volume [6]. The main limitations are heat and mass transfer which originate from low thermal transport and uptake capacity of active sorbent materials under the operating conditions [7-10]. Therefore, the performance of ACS systems significantly relies on properties and effectiveness of the adsorbent-adsorbate working pairs [11].

To overcome the limitations of the current sorbents, synthesis of new composites - featuring additives to improve heat transfer properties, operational cycles and/or overall power densities - have received great attention [8, 12]. In previous studies in our lab, we established that thermal diffusivity ($\alpha = {k}/{\rho C_p}$), which is a combination of thermal conductivity (k), specific heat (Cp) and density (ρ) is the key parameter for improving SCP [13]. Demir et al. studied the effect of different metal particle additives to improve thermal conductivity of unconsolidated silica gel bed [14]. In another work, Saha et al. reported that addition of metallic fillers up to 30 wt.% could enhance thermal conductivity and SCP [6]. Fayazmanesh et al. evaluated the effect of graphite flakes (GF) as thermal conductive additives to CaCl₂-silica gel composites [15]. Chan et al. studied the effect of adding carbon nanotube (CNT) to CaCl₂-zeolite. They concluded that addition of CNTs can enhance the thermal conductivity while it doesn't have noticeable effect on uptake capacity of the composites [16].

The present study investigates the effect of GF and CNTs as combined conductive additives on thermal conductivity and thermal diffusivity of CaCl₂-silica gel sorption composite materials.

Moreover, the uptake capacity is evaluated through water adsorption/desorption isotherms for two set of composites. To this end, our goal is to establish an optimum composition of $CaCl_2$-silica gel-conductive additives composites to improve SCP in ACS. The SCP of the targeted composite sorbents are discussed elsewhere [17].

Results and Discussion

Sorbent material preparation

Among sorbent materials suggested for water sorption cooling systems, $CaCl_2$ in mesoporous silica gel has been reported as one of the most promising solid sorbent composites [3]. The focus of this study is modification of consolidated $CaCl_2$-silica gel composites by addition of varying concentrations of GF and CNT and compare their effectiveness. The silica gel is SiliaFlash B150 with 250-500 μm irregular shaped grains and average pore diameter of 15 nm, purchased from Silicycle, Inc., Quebec, Canada. $CaCl_2$ was added to silica gel in 1:1 weight ratio. Then the thermally conductive additive which is either GF or CNT were added in weight percentages between 0 and 20 wt.%. Graphite flakes (150 lm, 332461 Sigma-Aldrich), has a thickness of ≥150 μm with width of graphene sheets between 50-800 μm. The CNT is an industrial grade of multiwall carbon nanotube from Nanolab, USA with 5-20 μm nominal length and 10-30 nm diameter. Polyvinylpyrrolidone, 40,000MW (PVP-40), purchased from Amresco Inc., US, was used as binder. For the consolidated composite preparation, a total amount of 10 wt.% of the binder was dissolved in water. Then the aqueous solution of PVP-40 was added to the powder mixture of silica gel, $CaCl_2$ and either GF or CNT. The slurry composites were dried at the oven at 80 ⁰C for 5 hours, and then baked at 120 ⁰C for another 5 hours to produce the consolidated material.

Analyses and characterization

To compare the performances of the targeted additives, thermal transport and uptake characteristics are measured for the composites. The composites with 5 wt.% concentration of CNT and GF were chosen as representatives of the composites to study the effect of different additives on pore volume, surface area, and the morphology of the composites. Then, composites with various amount (0 to 20 wt.%) of conductive additives are considered in the next section to evaluate the thermal transport properties. Total pore volume and specific surface area of the composites, as listed in Table 1, were calculated based on nitrogen sorption isotherms of the samples collected with a volumetric physisorption analyser (ASAP 2020, Micromeritics Instruments). The samples were dried prior to the tests under vacuum at 150 °C for 1 hour followed by 2 hours at 200 °C. The specific surface area (S_{BET}) was calculated using the Brunauer, Emmett and Teller (BET) model while the pore volume was calculated from the adsorption curves at highest relative pressures (~ 0.98) using the Barrett, Joyner and Halenda (BJH) model [18, 19]. According to the porosity characterization results, both surface area and pore volume were slightly higher for the CNT sample compared to that of the GF sample. This could be attributed to the geometry and size of the additive particles and their interaction with the host matrix. The combination of higher surface area and smaller particle size of CNTs, (0.01-0.03) x (5-20) μm versus (50-800) x (≥150) μm for GFs, leads to more available surface and less possible pore-plugging with CNTs compared to GFs.

Scanning electron microscope (FEI/Aspex-Explorer) images (Figure 1) show the dispersion of 5 wt.% of GF and CNT inside the silica gel-$CaCl_2$-binder composites. SEM images indicate notable

changes in the morphology and binder structure as a result of GF and CNT addition. It seems that the CNTs are more engaged with the polymer binder and are concentrated within the polymer matrix while GFs are most likely exist as stacks and are distributed throughout the composite. Therefore, it is expected that mechanical and thermal transport properties of the composites with the mentioned additives would be different due to different interactions and morphologies of the components.

Table 1- Surface area and pore volume of composites

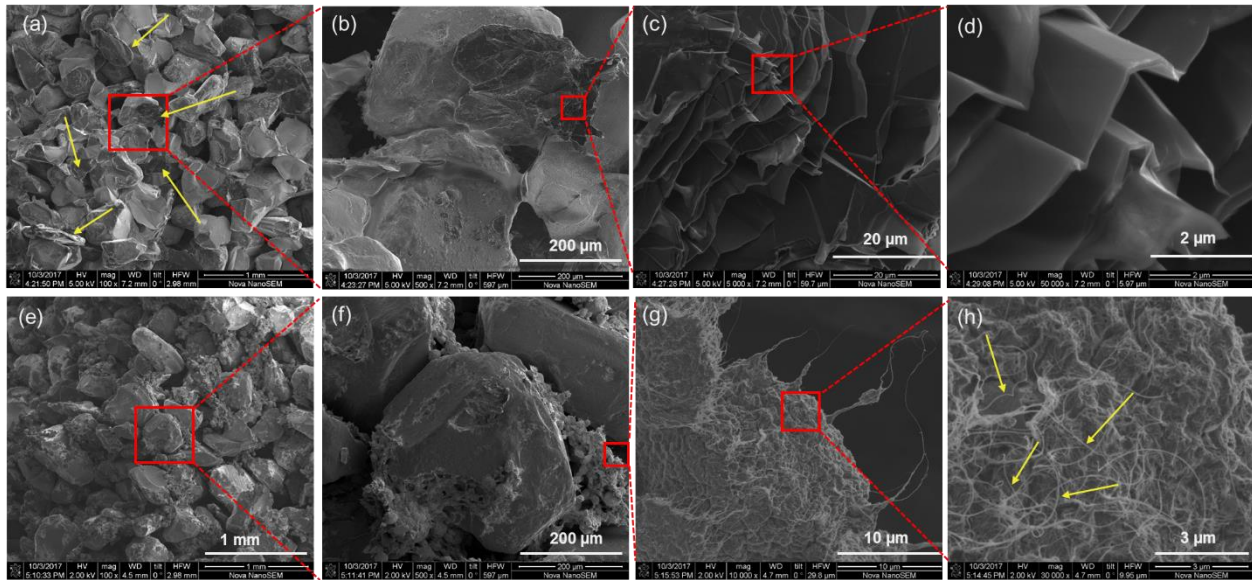| Sample	Composition (wt.%)					S_{BET} (m²/g)	Total pore volume (cm³/g) at P/P$_0$= 0.98
	PVP	Silica Gel	CaCl$_2$	Graphite flakes	CNT		
PVP-SG-CalCl$_2$-GF 5%	10	42.5	42.5	5	0	60	0.20
PVP-SG-CalCl$_2$-CNT 5%	10	42.5	42.5	0	5	66	0.23
PVP-SG-CalCl$_2$	10	45	45	0	0	270	1.13
Silica Gel (B150)	0	100	0	0	0	112	0.48

Figure 1. SEM images (a), (b), (c) and (d) PVP-SG-CaCl$_2$-5 wt.% GF, (e), (f), (g) and (h) PVP-SG-CaCl$_2$-5 wt.% CNT. Yellow arrows point at (a) graphite flakes and (h) CNTs dispersed in the composites

It is well known that thermal conductivity in a porous medium is a function of several factors including pore space, solid matrix properties, shape of components, and a percolation threshold [20]. Percolation threshold is a concept which determines the probability that fillers within a medium are sufficiently connected to form a conductive network [21]. Hence, it is important to consider the amount of the conductive additive relative to the available volume for their dispersion in the composite. While the amount of conductive additives should be enough for building a "conductive network" within the composite, the volume should be large enough to give the conductive additives sufficient space to form the conductive network structure. When certain free volume is available within the composite, conductive additives should be added up to a percolation threshold to make the material thermal conductive. Since this threshold depends on the size and

shape of the conductive additive, it would be different for CNT versus GF particles. We would see the effect on conductivity performance of the samples in the following section.

To evaluate the effect of addition of the targeted conductive additives (CNT and GF) on the thermal conductivity and diffusivity of the composite samples, these properties were measured using a transient plane source (TPS) "hot disk" thermal constants analyzer (TPS 2500S, ThermTest Inc., Frederiction, Canada) as per ISO 22007-2 [22]. A Kapton encapsulated double spiral nickel wire sensor (design #5465) with a 2 mm radius, was used for both transient heating of the sample and as precise resistance thermometer for simultaneous temperature measurements. The sensor was placed between a pair of identical samples. During TPS measurements, constant temperature difference develops at the sample-sensor interfaces as a result of contact resistance between the sensor and sample surface. The effect of this constant temperature difference on the measured sample properties was de-convoluted in the calculations [15].

In Figure 2, thermal conductivity and diffusivity results reveal that addition of conductive additives improves thermal transport; e.g. up to 376% higher conductivity and 483% higher diffusivity for sample with 20 wt.% of GF, and up to 90% higher conductivity and 95% higher diffusivity with 15 wt.% of CNT. Figure 2a shows that both thermal conductivity and thermal diffusivity change linearly with the GF content. New correlations are proposed for thermal diffusivity (α) and thermal conductivity (k) as a function of GF wt.% below:

$$k = 0.1267 + 0.0176 \times GF\% \qquad\qquad eq.1$$

$$\alpha = 0.1133 + 0.0572 \times GF\% \qquad\qquad eq.2$$

One can conclude that addition of GF would linearly increase thermal transport properties as the GF particles are dispersing and forming conductive networks within the composites without agglomerating in a specific part. We can see a thermal percolation threshold at ~ 10 wt.% of GF at which the increase in thermal diffusivity is more pronounced. However, as Figure 2b shows, there is not such a linear trend for increasing thermal diffusivity and conductivity by CNT addition at concentrations above 5 wt.%. Although there is a kind of percolation threshold at ~ 5 wt.% for CNTs, this is an optimum concentration for CNTs and no significant improvement is achieved by adding more CNT content beyond this concentration. The reason is that CNTs are more likely agglomerate in the binder matrix, as shown in SEM images (Figure 1, e-h). Therefore, extra CNTs within the same amount of binder wouldn't have enough space to form a network to conduct heat in the composite. Consequently, the excessive amount of CNTs might interfere with the network formation and negatively impact the heat conduction. In conclusion, the difference in the effect of conductive additives and their percolation loading is attributed to their different interaction with the other components in the composite specifically the binder.
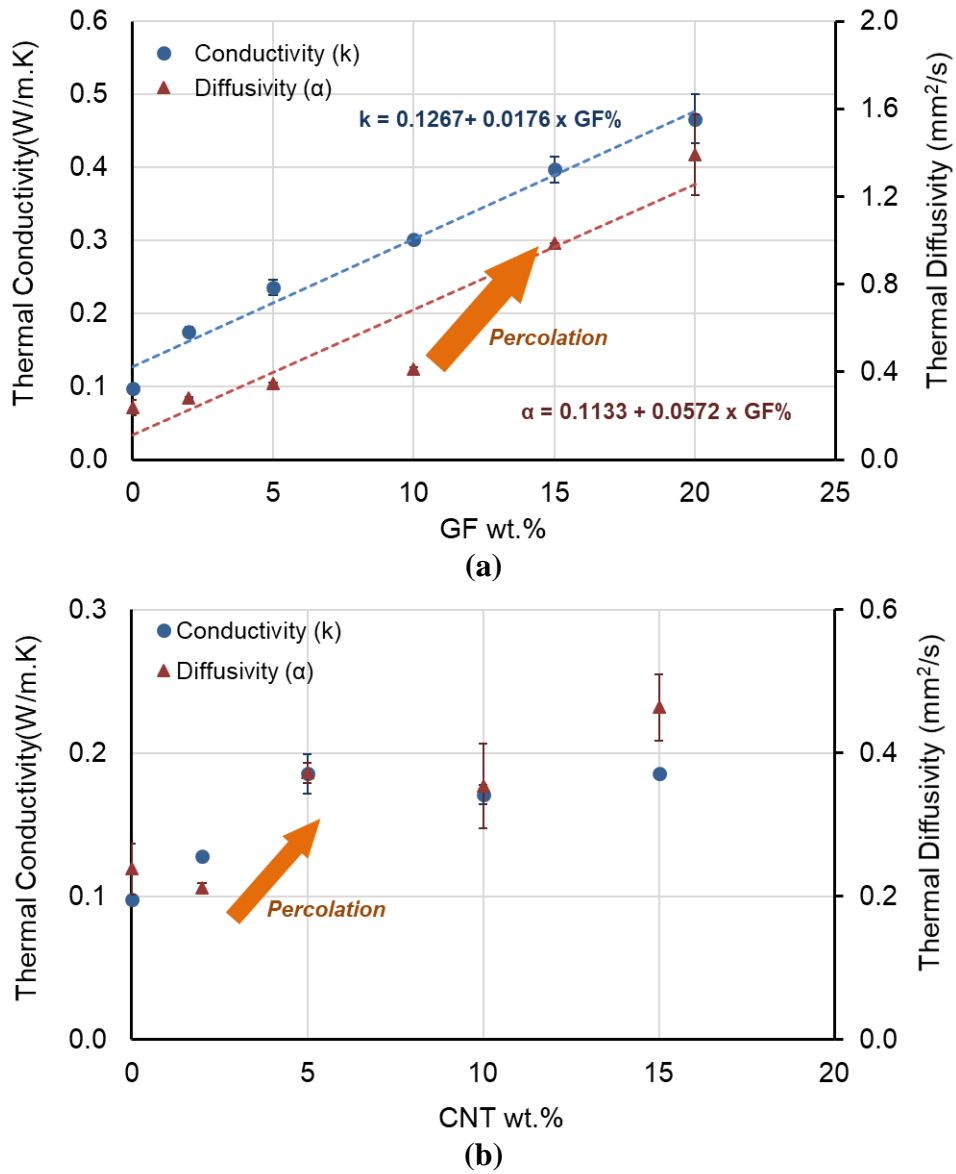
Figure 2. Thermal conductivity and thermal diffusivity of composites with (a) GF and (b) CNT

The other key factor for the choice of sorbent material is the uptake capacity. According to literature, further studies are still required to find optimal compromise(s) between heat and mass transfer properties of the solid sorbent material [3]. As such, water sorption isotherms were evaluated using a thermogravimetric vapor sorption analyzer (IGA-002, Hiden Isochema) available in our lab at 0.04–2.84 kPa with the pressure step of 0.2 kPa at 25°C. Confirmed with water uptake isotherms in Figure 3, there is no significant change in the uptake capacity of the composites at 5 wt.% concentration of either GF or CNT in comparison with the sample without conductive additives. This can be used to develop new composites with increased thermal conductivity (up to 140%) and thermal diffusivity (up to 56%) with negligible impact on uptake capacity. However, the composites with larger amount of conductive additives would have less

water uptake due to less active sorbent material content, as expected. Therefore, optimal compromise for water sorption capacity and thermal transport properties should be found according to the specific operation conditions.
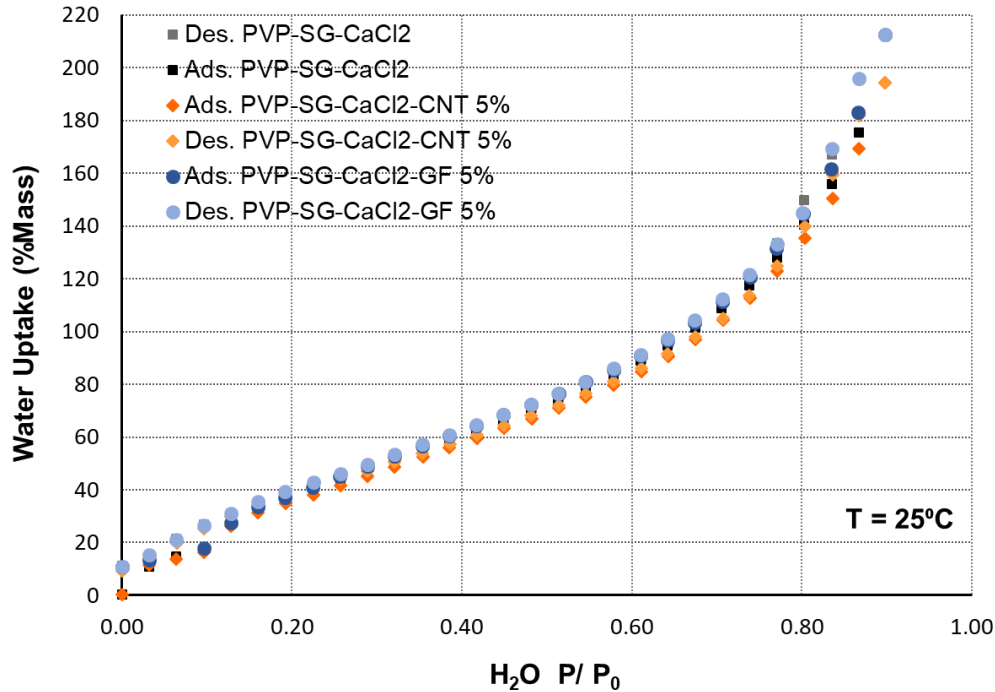

Fig 3. Water uptake isotherms of composites with 0 and 5 wt.% of GF and CNT.

Summary and Conclusion

Two sets of consolidated composites with various loadings of GF and CNT were prepared to evaluate the effect of different conductive additives on the performances of sorbent materials. Results confirm that there are differences in the effect of CNT and GF on the structure, thermal transport and uptake characteristics of the composites due to their different geometry, morphology, and interaction within the composites. In this study, dependence of percolation threshold and effectiveness of the thermally conductive additives on shape and dispersion of the particles within the consolidated sorbent composites has been discussed. In addition, minimal negative effect on water uptake capacity was observed when 5% CNT or GF were added to $CaCl_2$-silica gel composites, while 90 to 140% and 56 to 45% improvement on thermal conductivity and diffusivity were measured, respectively. Further studies for optimal type, shape and amount of conductive additives is required.

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