GRAPHITE-DOPED COMPOSITE ADSORBENT COATINGS FOR HEAT-DRIVEN WATER SORPTION COOLING SYSTEMS

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Abstract

Thermally driven adsorption cooling systems can reduce the primary energy demand for air conditioning and refrigeration systems. Major challenges facing coated adsorption cooling systems include: low thermal conductivity, limited durability, control of coating thickness, and maintaining high adsorbate uptake. The overall performance of adsorption cooling systems can be improved by new composite materials and coatings developed to improve heat and mass transfer. In this study, silica gels with surface areas (S_{BET}) of 494 $m^2 \cdot g^{-1}$ were soaked with a salt and bindersolutions to produce adsorbent coatings. The properties of the coated materialswere evaluated by porosimetry and transient plane source thermal properties analysis. The thermal conductivity of the composite adsorbent coating was improved by adding graphite flakes with varying weight percentages. Thermal conductivity of the composite coating increased from 0.1 $W \cdot m^{-1} \cdot K^{-1}$(0 wt%graphite flakes) to 0.3$W \cdot m^{-1} \cdot K^{-1}$ (20 wt% graphite flakes); up to 230% enhancement in thermal conductivity of graphite-doped samples were obsrerved. Such significant enhancement in thermal conductivity can lead to considerable improvement in heat transfer in sorption bed, which in turn can lead to more compact sorption bed design and improved overal effeiciency and specific cooling capacity of any adsorption cooling system. Water uptake and multi-cycle performancestudies of the composite coating material were performed under adsorption cooling cycle conditions using a thermogravimetric vapour sorption analyser.

KEYWORDS

Adsorption cooling,adsorbent coating,surface characterisation, water vapour sorption, thermal conductivity

INTRODUCTION

In the early 1900s,ammonia/$CaCl_2$ and methanol/activated carbon adsorption cooling systems were developed and commercialized for industrial and residential use[1][2], including mobile systems such as a SO_2/silica gel system for the transportation of frozen fish by rail [3]. Shortly thereafter, cheap vapour-compression cycle refrigeration systems using toxic refrigerants and electrical motors conqueredthe commercial marketand sorption cooling systems disappeared for over 60 years[4]. Thisdevelopmentstagnation lasteduntil concerns over ozone layer depletion, the energy consumption of compressors, and the role ofgreenhouse gas emissions, including hydrofluorocarbon refrigerants and CO_2, in climate changebecame a concern[4].Sorption-cooling systems utilize environmentally friendly refrigerants such as water,lack moving parts, which leave the system silent and low maintenance, and cangenerate cooling power from low grade industrial waste heat or solar thermal energy.

Most adsorption cooling systems use a granular adsorbent in a packed bed design.These systems have high mass transfer rates, however high thermal resistance between granules and the heat exchanger surface remains a major challenge. Different methods to improve heat transfer have been investigated such as binding or synthesizing [5]adsorbentonto the heat exchanger surface[6], using consolidated bed techniques whereby sorbents and thermally conductive materials are compacted into a solid matrix [7], and coating a heat exchanger surface with a composite adsorbent. The first twomethods improve heat transfer performance, but decrease water uptake rate [8]. For coatings with composite adsorbents, the main issue is choosing a proper binder composition and concentration. Listed below in Table 1 are groups that are developing adsorption coatings using organic or inorganic binders.

It has been shown thathygroscopic salts confined in mesoporous silica gels have high adsorption rates with a regeneration temperature below 100°C[9][10]. Ponomarenko et al. prepared $CaCl_2$ confined in SBA-15 silica gel with water sorption capacity of 0.47 g/g at 50°C andwater vapor $P/P_0 < 0.3$[12]. In most cases, hygroscopic salts improve sorption performance but the physical properties of a prospective host matrix cannot be neglected [9]. Confinement of salt to a porous matrix with narrow pore size distribution has been reported with an improvement inwater uptake from 0.06 g/g for Fuji silica gel of type RD to 0.15 g/g for $CaCl_2$/SBA (11.8 nm) at a temperature drop from 60 to 35°C and a pressure of 1.23 kPa[13].

The thermal conductivity of sorbentshas a great impact on the dynamic performance of the sorption systems. Yu et al. showed that with increasing sorbed water content the thermal conductivity of $CaCl_2$-KSK increased from 0.13 $W\cdot m^{-1}\cdot K^{-1}$ to 0.5 $W\cdot m^{-1}\cdot K^{-1}$[14]. Heat transfer enhancement can be also achieved by binding or synthesising adsorbent on the surface of the adsorber bed [15][16] or by physically mixing adsorbent material with high thermal conductivity materials such as metal powders, metallic foams, graphite,or carbon fiber[17]. Istituto et al. observed that zeolite with aluminum hydroxide had greater thermal conductivity than zeolite with graphite or PTFE(polythetrafluoroethylene) [17]**.** Thermal conductivity of composite adsorbents made using a sol-gel process with copper nano-powder were measured by the transient plane source (TPS) method and showed 20% enhancement in thermal conductivity compared to composites without additives [18]. Effective thermal conductivity of unconsolidated adsorbent improved from 0.106 $W\cdot m^{-1}\cdot K^{-1}$ to 0.363 $W\cdot m^{-1}\cdot K^{-1}$ by adding 15 wt% shaved aluminum [19].

Major challenges faced in coated adsorption cooling systems include material durability, coated material thickness, adsorption uptake and effective thermal conductivity. The overall performance of adsorption cooling systems can be improved by the development of new composite materials with high adsorbent uptake and increased heat and mass transfer properties. Tothis end, in this study several $CaCl_2$/silica gel composites were prepared with organic binders and thermally conductive additives. The surface area and pore size distribution were examined.Water uptake and multi-cycle performance of our samples at different temperatures were measured andthe thermal conductivity of the composite adsorbents and a loose grainsample with different thermally conductive additive concentrationswerestudied.

EXPERIMENT

Sample Preparation

Composite adsorbents were prepared utilizing chromatography-grade commercial silica gel Silicycle,

Table 1. Composite coating adsorbent reported in literature

Composite	Coating technique	Water sorption tests	Results	Ref
SAPO34 (Zeolite adsorbent) and 10% binder (N-propyl-trimethoxy-silane)	Dip coating	30-150°C 11 mbar	• S-shape isotherm • SAPO34: ~27 wt% water uptake at 30 °C, ~25 wt% uptake for 10 wt% binder sample	5
Mitsubishi AQOA-Z02 and 15 wt% clay based binder	1. MPI coating (by Mitsubishi Plastics) 2. ITAE coating by CNR-ITAE)	20-160°C 10, 25 mbar	• S-shape isotherm • Uptake at 20 °C, 10 mbar: AQOA-Z02 ~26 wt%, MPI coating ~24 wt%, ITAE coating ~24 wt%	23
Silica gel and 0.5-1 vol.% tetraethyl-orthosilicate binder	Electrophoretic deposition (EPD)	25°C P/P_0=0-1 (31 mbar)	Uptake at P/P_0~1: • Silica gel:~ 0.5 g/g • TEOS free silica gel:~0.48 g/g • 0.5 v% TEOS silica: ~0.48 g/g • 0.1 v% TEOS silica:~ 0.4 g/g	24
Aluminiumphosphate(AIPO-18) and 6 wt% binder (polyvinyl alcohol)	Coating suspensions deposited by pipette on substrate	9-15°C 11.5, 17 mbar	• Mass flow decreases with increasing adsorbent thickness	25

Table 2. Composites prepared with SiliaFlash B60silica gel matrix

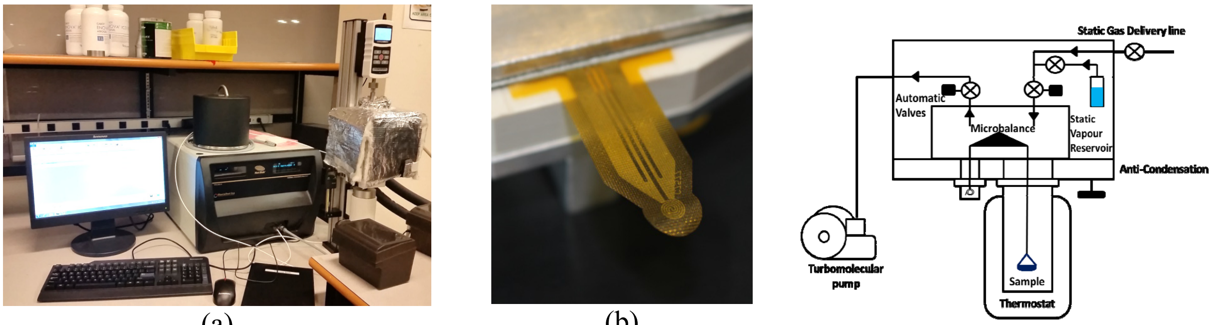
$CaCl_2$ wt.%	Additive	Binder	Designation
0	-	-	S6
28	-	-	S6-$CaCl_2$
28	-	PVP10	S6-$CaCl_2$-PVP10
28	-	PVP40	S6-$CaCl_2$-PVP40
0	Graphite flakes	-	S6-G
0	Graphite flakes	PVP40	S6-PVP40-G
28	Graphite flakes	PVP40	S6-$CaCl_2$-PVP40-G

Inc (Quebec, Canada) with irregular shaped grains with average particle diameters of 0.2-0.5 mm and average pore diameters of 6 nm. In batches of 100 g, the dry mesoporous silica was wetted with ethanol. An aqueous solution of $CaCl_2$ andpolyvinylpyrrolidone (PVP)(PVP-10, 10,000 MW, Sigma Aldrich and PVP-40, 40,000 MW, Amresco) binder(Table 2) was added andthe slurrywas placed on open trays in a fume hood to dry for 24 hours. The damp materials were then baked at 180°C for over 2 hours. The composition and volume of solution added to the silica was such that complete deposition of the salt and binder into the mesoporous silica produced a product with 28 wt% $CaCl_2$and 15 wt% PVP. Dry silica particles in 4 g batches were used to prepare a range of composites by combining silica with binder (15 wt% product) and thermally conductive graphite flakes (150 µm, Sigma Aldrich). These composites were prepared both with and without $CaCl_2$. The slurrieswere baked for one hour at 50°C until damp or dry, and then heated to180°C for one hour to cross-link the binder.

Characterization

To determine the specific surface area (S_{BET}), average pore diameter (D) and pore volume (V),of thesilica gel and silica gel composite samples, nitrogen sorption isotherms at -196˚C were collected with avolumetric physisorption analyser (ASAP2020, Micromeritics Instruments).Prior to testing, the samples weredried under vacuum at 150˚C for 1 hour, followed by 2 hours at 200˚C. The S_{BET} was calculated from the Brunauer, Emmett and Teller (BET) model while the Barrett, Joyner and Halenda (BJH) model was used to calculate the incremental pore volume from the adsorption curves[20][21].The composite microstructure wasimaged with a scanning electron microscope (FEI/Aspex-Explorer) at room temperature with beam energy of 10KeV.

Thermal conductivity, thermal diffusivity and specific heat of the samples were measured at room temperature with a transient plane source (TPS)thermal constants analyser, Fig.2a (TPS 2500S, ThermtestThermophysical Instruments). The2 mm radiusdouble spiral "hot disk" nickel sensor, Fig.2b was placed between two identical samples,and1 kgfwas applied to ensure good contact. Each composite sample was tested fivetimes at each of three positions and the results wereaveraged.



(a) (b) (c)

Fig.2. a) TPS thermal constants analyzer. b) Double spiral "hot disk" nickel sensor. c) Thermogravimetric sorption analyzer schematic.

Table 3. Surface characteristics of silica gel and silica-supported $CaCl_2$ composites

Sample	$\boldsymbol{S_{BET}}$ **(m^2/g)**	$\boldsymbol{V}$ **(cm^3/g)**	$\boldsymbol{D}$ **(nm)**	**Product Specifications** $\boldsymbol{S_{BET}}$**, V, particle size**
S6	494	0.77	4.8	514 m^2/g, 0.75 cm^3/g, 0.2-0.5mm
S6-$CaCl_2$	134	0.31	7.0	—
S6-$CaCl_2$-PVP10	91	0.15	4.8	—
S6-$CaCl_2$-PVP40	102	0.21	6.1	—

Water sorption isotherms (0-27 mbar) for the composite adsorbents were measured using athermogravimetricanalyzer, a schematic is shown inFig.2c,(IGA-002, HidenIsochema)at 25, 35 and 78°C. Prior to water sorption tests, the samples were dried under vacuumfor 6 hours at 90°C and the dry masses wererecorded.

RESULTS AND DISCUSSION

Pore-size distribution

The differential pore volume distribution of the silica and composite samples were obtained through analysis of the adsorption branch of the N_2 isotherms and is shown in Fig.3a.As summarised in Table 4, the 28 wt% $CaCl_2$was distributed within the silica gel pores, decreasing the S_{BET} and V, and increasing the average pore diameter from 4.8 to 7 nm. Comparing samples S6-$CaCl_2$-PVP10 and S6-$CaCl_2$-PVP40, the surface area and pore volume decreased significantly for the sample containing PVP-10, the lower molecular weight binder.The SEM images of loose grain silica gel, S6, and S6-CaCl2-PVP40 composite shown in Figure 2b-c, indicate that the binder does not fill the voids between silica gel particles.

Water Vapour Sorption

The water sorption properties of sorbents with PVP-10 and PVP-40 binders were measured at 25, 35 and 78°C, as shown in Figure 3.For S6-$CaCl_2$-PVP40,the water uptake at 34.7°C and 24 mbar was0.41 g/g while for S6-$CaCl_2$-PVP10 it wasonly 0.32 g/g. The greater infiltration of the pore structure by the lower molecular weight PVP-10 (Table 3) has a negative impact on adsorption.

The difference in equilibrium water content of the samples under operational cycle conditions for adsorption (12 mbar, 35°C) and desorption (27 mbar, 80°C) are summarized in Table 4.There was no loss in the water uptake capacity of the active materials in the sorbents containing 15 wt%binder. This reduction observed is consistent with the binder content only. PVP is a hygroscopic binder with water uptake of up to 6.6 wt% at 12 mbar, 35°Cfor the bulk material. The 35°Cwater sorption isotherms for the samples are

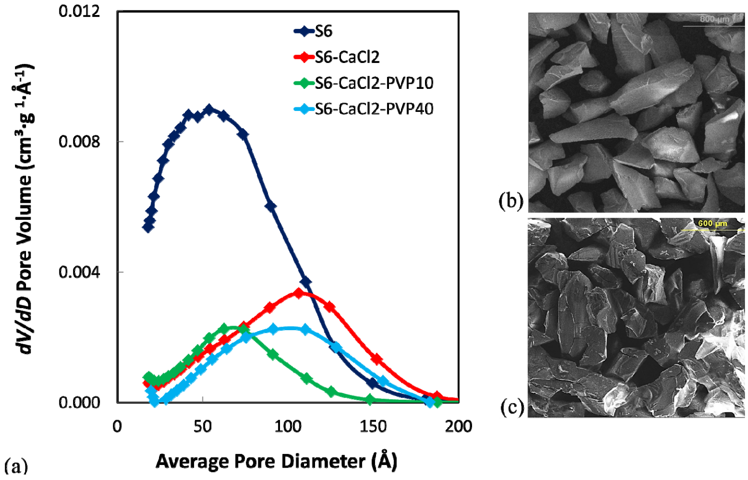


Fig.3. a) Pore size distribution plots for silica gel and composites from N_2 adsorption isotherms fit with BJH model utilizing Hasley: FAAS statistical thickness curves. SEM images of (b) loose grain S6 (c) S6-$CaCl_2$-PVP40

plotted in Figure 4 in grams per gram of composite material including the non-adsorbing thermally conductive graphite flake additive. The water uptake of samples with thermally conductive additives reduced while by considering the amount of active material the water uptake remain the same and no loss can be seen in the performance.

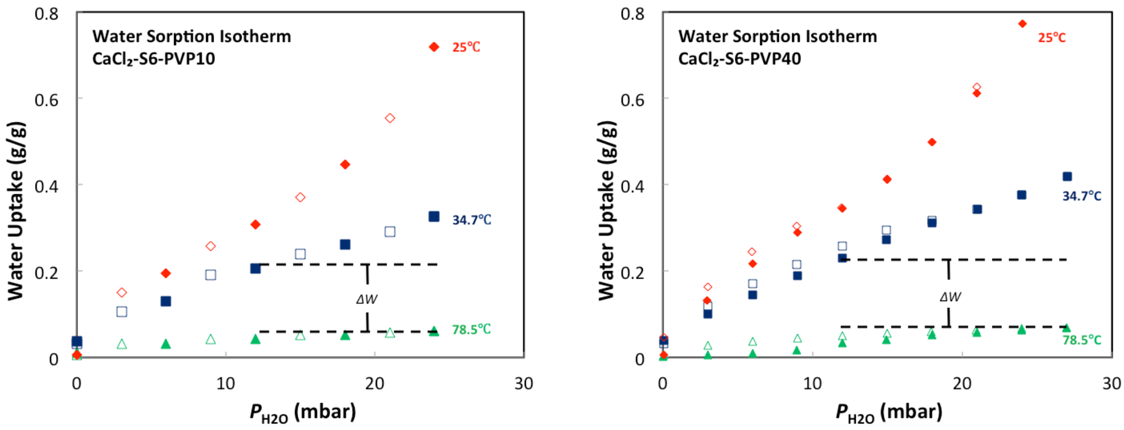


Fig.3. Water uptake with respect to pressure in shown for (a) S6-$CaCl_2$-PVP10 and (b) S6-$CaCl_2$-PVP40

Table 4. Sorption cycle equilibrium uptake.

Sample	**H_2O uptake capacity (mass%)**		**Δw**
	35 °C, 12 mbar	80 °C, 27 mbar	**(mass%)**
S6	5.4	2.0	3.4
S6-$CaCl_2$	33.4	10.8	22.6
S6-$CaCl_2$-PVP10	20.5	4.3	16.2
S6-$CaCl_2$-PVP40	23.0	3.3	19.7

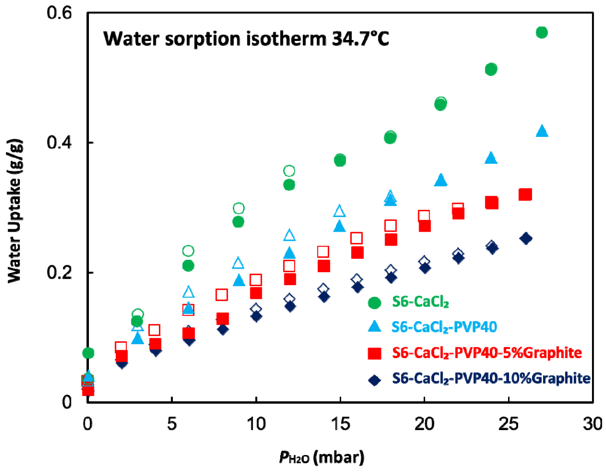


Fig.4. Effect of addtives (binder and thermal condutive material) on water sorption capacity.

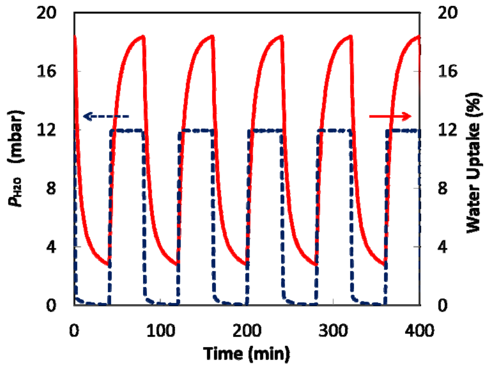


Fig.5. Five pressure swing adsorption-desorption cycles of S6-$CaCl_2$-PVP40 at 35°C

Table 5. Multi-cycle performance of S6-$CaCl_2$-PVP40

T	**Cycle number**	**H_20 uptake (mass%)**
25°C	1 10 20 150	28.1 28.5 29.0 29.2
35°C	160 300	18.4 18.1

Multi-cycle Performance

The adsorbent compositeS6-$CaCl_2$-PVP40 was selected for durability testing.The sample was dried for 6 hours at 90 °C under vacuum at the beginning of the test. The thermogravimetric analyzer was then programmed to run pressure swing cycles, exposing the sample to 12 mbar H_2O for 40 minutes and then drying the sample under vacuum for 40 minutes. The sample weight was monitored for 150of these sorption cycles at 25°C,followed by 150 at 35°C. Fig.5shows thepressure and water uptake for fivesorption cycles for S6-$CaCl_2$-PVP40. In Table 5, the adsorption capacity of samples at both temperatures is shown to be consistent for 150 cycles.

Thermal conductivity

The thermal conductivity of the composite adsorbent material is increased with the addition of graphite flakes as shown in Fig. 6. Graphite flakes could be seen to have dispersed evenly in the composite adsorbent. The thermal conductivity of composite material improved from 0.13 $W{\cdot}m^{-1}{\cdot}K^{-1}$ (0 wt% graphite flakes) to 0.3 $W{\cdot}m^{-1}{\cdot}K^{-1}$ (20 wt% graphite flakes), approximately a 230% enhancement. The addition of hydroscopic salt and binder to the composite adsorbent also increased the thermal conductivity.

CONCLUSION

Composite adsorbent coatings were prepared from binders with different molecular weights,and their water uptake capacities were measured. The water uptake of the composites with the lower molecular weight

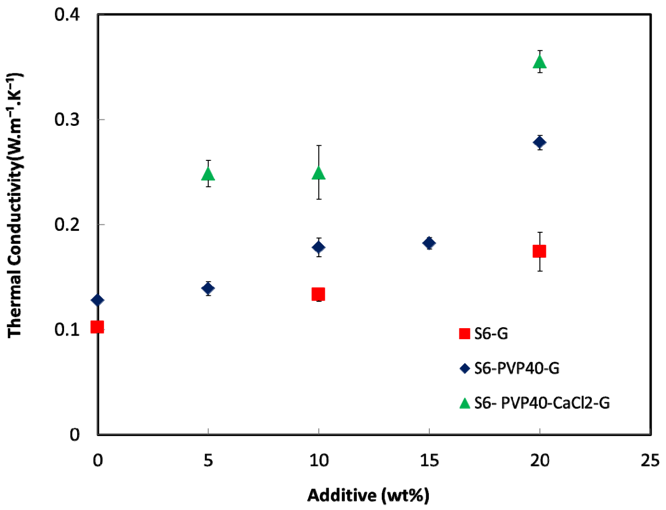


Fig.6. Thermal condutivity comparison of composite adsorbent coatings with different addtives

binder was 32.7 g/g (26 mbar, 34.7°C) while for composite with higher molecular weight binder under the same conditionsit was 37.6 g/g.Water uptake and thermal conductivity of composites with and without $CaCl_2$ and thermally conductive additives were measured.A huge 230% enhancement in thermal conductivity can lead to significant improvement of sorption bed design and reduction of the size and foot print of sorption cooling systems.

Nomenclature

BET	Brunauer, Emmett and Teller model	
BJH	Barrett, Joyner and Halenda model	
TPS	Transient plane source	
D	average pore diameter	(nm)
S	specific surface area	(m^2/g)
V	pore volume	(cm^3/g)
W	water uptake	(g/g of sorbent)

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