$CaCl_2$-silica gel consolidated with polyvinylpyrrolidone and graphite flakes for water-based adsorption cooling systems

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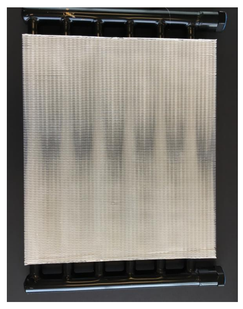
Introduction

Thermally-driven sorption chillers operate by cycling the temperature of adsorbent filled heat exchangers (HEx). Coating adsorbent on the HEx reduces thermal contact resistance, which can improve adsorption kinetics.

However, if the coating is thin more adsorber bed volume will be used by fins. Also, the lower the weight ratio of adsorbent to HEx, the greater the 'dead weight' thermal inertia of the system. By increasing the thickness of the coating, the thermal inertia of the HEx relative to the adsorbent can be reduced.



Finned-tube HEx coated with sorbent

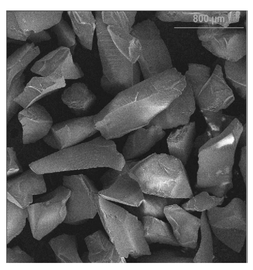
This study measures the sorption properties of high loads of $CaCl_2$ in silica gel consolidated with 10-15%wt binder and 20-25%wt graphite flakes, including composite sorbents coated on graphite sheet.

Methods

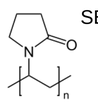
Sample Preparation

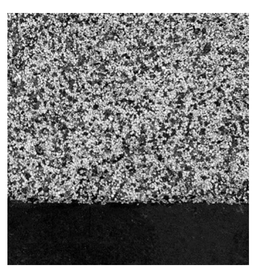
Composite sorbents were prepared by combining:

- Mesoporous silica gel, SiliaFlash® B150 (Silicycle Inc., Quebec), with irregular grains (250-500 μm) and 15 nm average pore diameter
- $CaCl_2$ dried at 200°C prior to weighing
- 40,000 MW polyvinylpyrrolidone (binder)
- Graphite flakes
- Sorbent composites were prepared with 0.4:1, 1:1, 1.4:1 and 2:1 weight ratios of $CaCl_2$ to silica gel, 25%wt graphite flakes and 15%wt PVP. Samples 4 mm and 8 mm thick were dried in 5 cm diameter molds for TPS and TGA tests.
- For "fin" tests, a thick aqueous slurry was prepared and applied to roll embossed graphite sheet (2 g/cm³) using a doctor blade approach to create coatings 1.4, 1.7, 2.5, and 3.3 mm thick containing 35 wt% $CaCl_2$, 35 wt% silica gel, 20 wt% graphite flakes, and 10 wt% PVP. The coated areas were 60 mm x 60 mm.

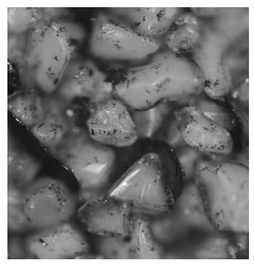


SEM image of silica gel





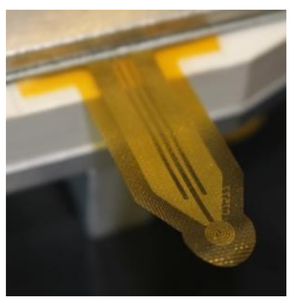
Optical image of composite sorbent on graphite



Optical image of composite

Material Characterization

- Surface area and pore size: Nitrogen isotherms
- Water sorption: Thermogravimetric vapor sorption analyzer
- Thermal conductivity: Transient plane source "hot disk" thermal constants analyzer

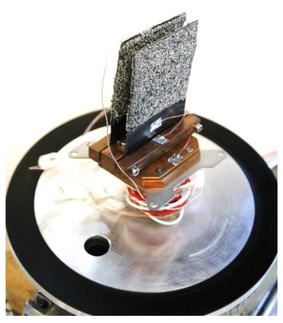


Transient plane source (TPS) thermal constants analyzer with "hot disk" nickel wire sensor and environmental chamber

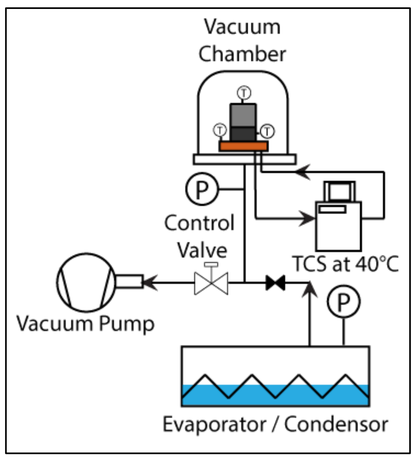
Thermogravimetric vapor sorption analyzer with active pressure control

Sorption Kinetics of Coatings on Graphite

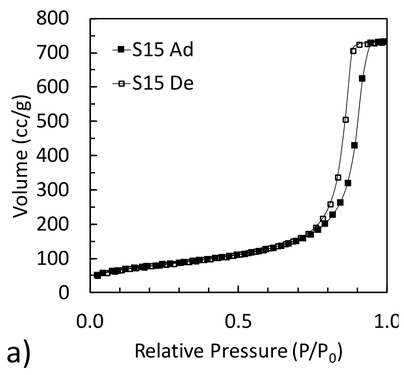
- A gravimetric "fin" tester was constructed to measure the uptake kinetics of composite sorbents coated on metal or graphite fins clamped horizontally or vertically to a temperature controlled copper plate heat exchanger. The samples are exposed to vapor pressure changes while their temperature and water uptake are recorded.
- The preliminary tests were conducted with T_{HEx} = 40°C, and the vapor source at 1°C (6.5 mbar) and 20°C (23.3 mbar)

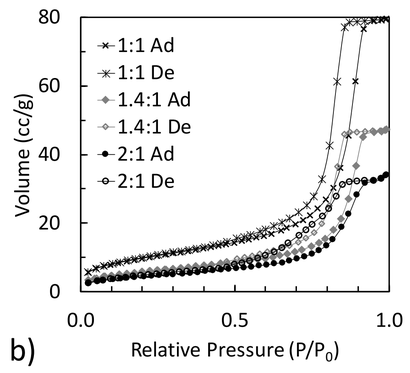


Custom-built gravimetric "fin" tester with two coated graphite sheets clamped to the heat transfer plate



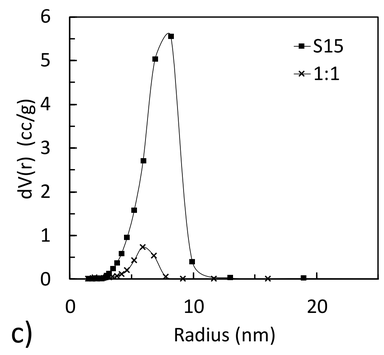
Material characterization





Porosimetry

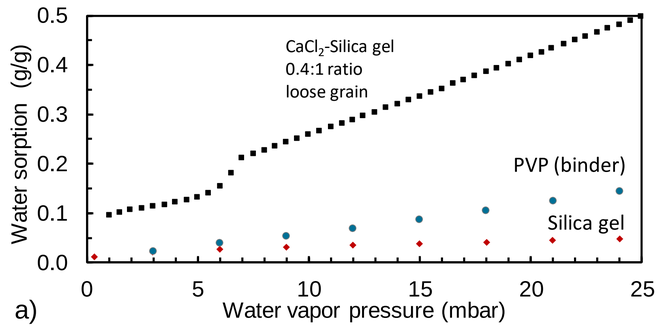
Nitrogen sorption isotherms of a) loose grain silica gel and b) composites with 1:1, 1.4:1, and 2:1 $CaCl_2$ to silica gel ratios, graphite flakes and binder. c) Pore size distribution for loose grain silica gel compared to a composite with a 1:1 $CaCl_2$ to silica gel ratio, 25%wt graphite flakes and 15%wt PVP.

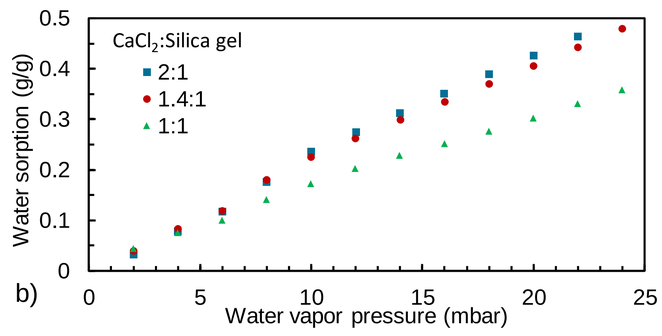


The isotherms are type IV and feature a hysteresis loop generated by capillary condensation in the mesopores. The surface area (S_{BET}) and pore volume decrease as the salt to silica gel ratio increases.

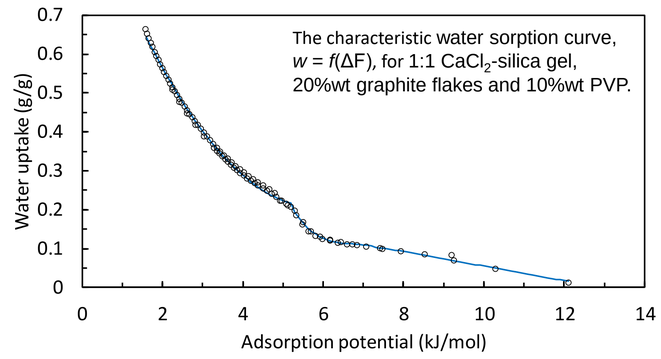
$CaCl_2$ to silica gel ratio	$CaCl_2$ (wt%)	Silica gel (wt%)	Graphite (wt%)	PVP (wt%)	S_{BET} (m^2/g)	Pore vol. (cc/g)	Pore vol. (cc/g_{silica})	Water uptake (g/g)
0:1	0	100	0	0	271	1.11	1.11	0.034
0.4:1	28	72	0	0	136	0.60	0.83	0.286
1:1	35	35	20	10	64	0.22	0.62	0.301
1:1	30	30	25	15	36	0.12	0.41	0.202
1.4:1	35	25	25	15	21	0.07	0.28	0.263
2:1	40	20	25	15	16	0.05	0.22	0.275

Table 1: Sample type, surface area, pore volume and water uptake at 12 mbar and 35°C.





Water adsorption isotherms at 35°C for a) loose grain samples of $CaCl_2$-silica gel, PVP and silica gel, and b) samples consolidated with 25%wt graphite flakes and 15% PVP containing $CaCl_2$ to silica gel ratios of 2:1, 1.4:1 and 1:1.



The characteristic curve from water sorption isotherm data at 25°C, 35°C, and 40°C replotted as a function of the adsorption potential, *ΔF*, also called the free energy of adsorption.

ΔF from 1.58 to 5.20 $\quad \Delta F = -RT\ln(h), h = {}^{P}/_{P_o}$
$w = 0.0247\cdot(\Delta F)^2 - 0.2867\cdot\Delta F + 1.0397$
ΔF from 5.2 to 7.5
$w = -0.0243\cdot(\Delta F)^3 + 0.4912\cdot(\Delta F)^2 - 3.3158\cdot\Delta F + 7.5864$
ΔF from 7.5 to 12.1
$w = -0.0187\cdot\Delta F + 0.2419$

Thermal conductivity of dry and wet composite samples

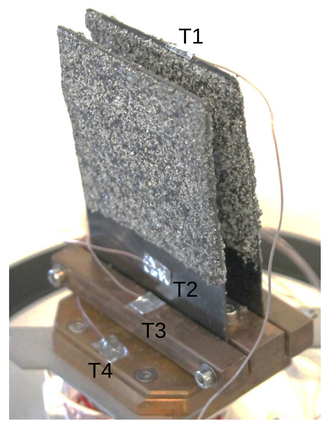
1:1 $CaCl_2$-silica gel 20wt% graphite flakes, 10wt% PVP	0% RH	20% RH
Thermal Conductivity (W m^{-1} K^{-1})	0.45	0.50
Thermal Diffusivity (mm^2 s^{-1})	0.28	0.25
Specific Heat (MJ m^{-3} K^{-1})	1.6	2.1

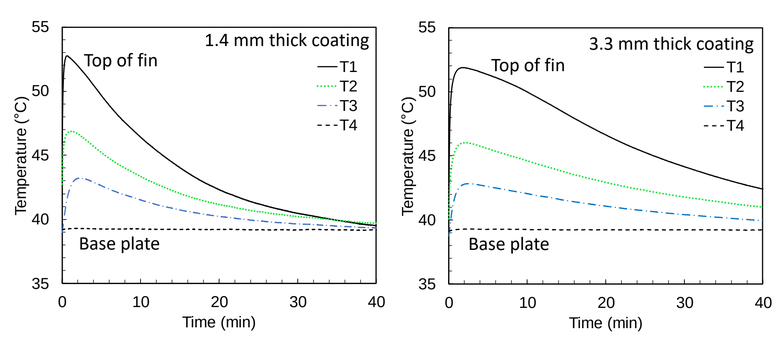
Gravimetric 'fin' tests

Adsorbent coated graphite sheet clamped to a water block. The adsorbent coating composition was 35%wt $CaCl_2$, 35%wt silica gel, 20%wt graphite flakes, and 10%wt binder.

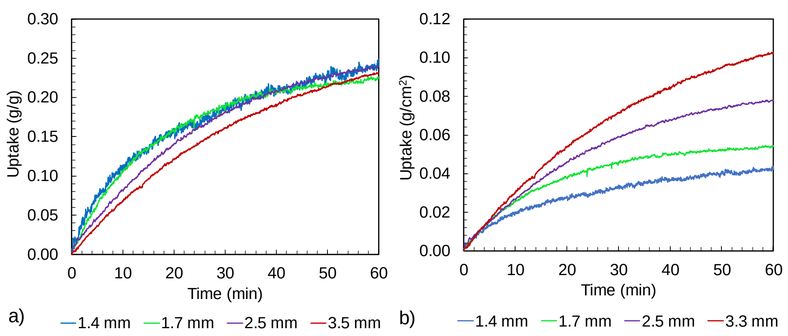
Preliminary tests of the uptake rate and temperature profile of sorbent coatings on graphite sheet were conducted.

Thermocouples were attached to the top and bottom of the graphite sheet, the clamp and the base plate. The tape used to apply the thermocouples did not adhere well to the sorbent coating.





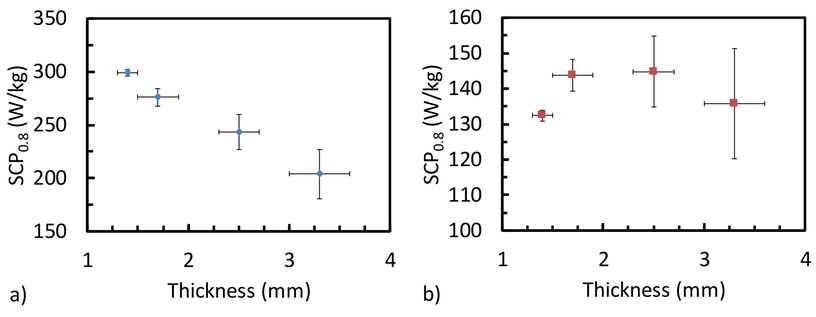
Temperature profiles at the top of thin (1.4 mm) and thick (3.3 mm) coated fins during adsorption.



Water uptake kinetics of sorbent coatings on graphite sheet a) per weight of sorbent and b) per adsorbent surface area. The thinner films had faster g/g uptake, however the thickest film had the fastest g/cm² uptake.

The potential specific cooling power for the samples is calculated from the rate of adsorption for 80% of the step in sorption uptake capacity at the operating conditions tested and the latent heat of vaporization of water.

$$SCP = \frac{\Delta w_{0.8} L_{v,20°C}}{\tau_{0.8}}$$



Specific cooling power a) per weight of adsorbent and b) per weight of adsorbent and substrate for 1.4 to 3.3 mm film thickness. The 1x60x120 mm^3 graphite substrates weigh ~8 g. The ratio of coating weight to fin weight varies from 0.8:1 to 2:1 as the adsorbent thickness increases from 1.4 to 3.3 mm for double sided coatings.

Conclusions

- Composites of $CaCl_2$-silica gel, graphite flake and PVP (binder) with high salt to silica gel loads were characterized, including a composite with greater water sorption capacity than loose grain 0.4:1 salt to silica gel ratio.
- In pressure-swing tests of coatings on graphite fins at 40°C, the 1.4 mm sample adsorbed nearly double the amount of the 3.3 mm per mass adsorbent at 10 minutes which is a common adsorption half-cycle time. However, the thicker sample had a greater uptake per area.

Support

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