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Research Paper

Consolidated adsorbent containing graphite flakes for heat-driven water sorption cooling systems

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HIGHLIGHTS

- New composite adsorbents were prepared by consolidating graphite flakes with silica gel using binders with different molecular weights.
- The 40,000 MW PVP binder had substantially less effect on the pore volume, pore size distribution and water uptake of silica gel-$CaCl_2$ composites than the 10,000 MW PVP binder.
- The water uptake of the silica gel-$CaCl_2$-PVP40 composite was consistent through 300 pressure swing cycles.
- The thermal conductivity of a set of S6-$CaCl_2$-PVP40 sorbent with 0–20 wt% graphite flakes were tested at 2 and 20 RH%.
- The effect of thermally conductive additives on water uptake and thermal conductivity studied.

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ABSTRACT

Thermally-driven sorption cooling systems can reduce the primary energy demand for air conditioning and refrigeration. The specific cooling performance (SCP) of an adsorption cooling system can be enhanced by increasing the heat transfer rate in a heat exchanger packed or coated with sorbent material. In this study, calcium chloride in a silica gel matrix was combined with a binder and graphite flakes to produce water absorbent consolidated composites. The characteristics of the composites were evaluated by porosimetry and transient plane source (TPS) thermal properties analysis. The addition of 20 wt% graphite flakes increased the thermal conductivity of the composite adsorbent from 0.57 $W\,m^{-1}\,K^{-1}$ to 0.78 $W\,m^{-1}\,K^{-1}$. Water sorption isotherms and vapor pressure swing durability tests were collected with a thermogravimetric vapor sorption analyser. Water uptake capacity 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. Water sorption during vapor pressure durability test was consistent within 28.5 and 18 wt% across 150 cycles at 25 and 35 °C.

1. Introduction

In the early 1900s, ammonia-$CaCl_2$ and methanol-activated carbon absorption cooling systems were developed and commercialized for industrial and residential refrigeration [1,2]; and mobile freezer systems with SO_2-silica gel as the adsorbate-adsorbent working pair were developed for the transportation of frozen fish by rail [3]. Shortly thereafter, cost effective vapor-compression cycle refrigeration systems using toxic refrigerants and electrical motors conquered the commercial market and sorption cooling systems disappeared for over 60 years [4]. This development stagnation lasted until the environmental costs of air conditioning and refrigeration, including the depletion of the ozone layer, the energy consumption of compressors, and the role of greenhouse gas emissions (hydrofluorocarbon refrigerants and CO_2) in climate change became a concern [4]. One of the sustainable and clean solutions for thermal management and heat storage is heat-driven sorption technology [5,6]. Sorption-cooling systems utilize environmentally friendly refrigerants, such as water, and can generate cooling power from low-grade industrial waste heat or renewable thermal energy sources (solar or geothermal).

The majority of commercial adsorption cooling systems use a granular adsorbent packed in a finned-tube heat exchanger [5,7,6]. However, the high contact thermal resistance between granules and the heat exchanger surface remains a major challenge [8]. Several methods to improve heat transfer have been investigated, such as synthesizing adsorbent on the heat exchanger surface [6], consolidating sorbents by compacting them with thermally conductive materials into a solid matrix [9], and coating

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Nomenclature

LDF	Linear Driving Force	t	time (LDF model)
BET	Brunauer, Emmett and Teller model	τ	characteristic time (s)
BJH	Barrett, Joyner and Halenda model	S	specific surface area ($m^2\ g^{-1}$)
RH	Relative Humidity	V	pore volume ($cm^3\ g^{-1}$)
SCP	specific cooling performance ($W\ g^{-1}$)	u(t)	water sorption at time t
TPS	transient plane source	Δu	total change in uptake
D	average pore diameter (nm)	w	water uptake (g/g of sorbent)
h_{fg}	water enthalpy of evaporation ($kJ\ kg^{-1}$)	$\Delta\omega$	total weight change (g/g of sorbent)
k	time constant		

a heat exchanger surface with a composite adsorbent [5]. The first two methods improve heat transfer performance, but can decrease water uptake rate [10]. For coatings with composite adsorbents, the main issue is choosing a binder composition and concentration without blocking pores.

Detail studies on hygroscopic salts confined to a porous host matrix have been done for sorption systems at the Boreskov Institute of Catalysis and ITAE/SNR in Messina, Italy [11]. Ponomarenko et al. prepared $CaCl_2$ confined in SBA-15 silica gel with water sorption capacity of 0.47 g/g at 50 °C and water vapor $P/P_0 < 0.3$ [12]. Temperature swing water sorption tests (60–30 °C) with vapor pressure of 1.23 kPa have been performed to compare CaCl2/SBA (mesoporous silica gel, average pore diameter 11.8 nm) with microporous silica gel (Fuji RD) under sorption system operating conditions. The $CaCl_2$/SBA has over twice the specific cooling power calculated from the measured sorption rate [13]. SWS-1L ($CaCl_2$ in mesoporous silica gel) demonstrated the coefficient of performance (COP) 0.6 at desorption as low as 85–95 °C in compare to silica gel-water and zeolite-water systems at low temperature heat generation [14]. Freni et al. provided a detailed comparative study on the most promising working pairs for thermal driven adsorptive heat pump, air conditioning and refrigeration applications [15]. For air conditioning and pumping purposes working with water as adsorbate, the highest heating/cooling COP up to 1.62/0.71 is reported for AQSOA-FAM Z02, LiBr-Silica gel and $CaCl_2$-Silica gel [15].

The thermal conductivity of sorbents has a great impact on the dynamic performance of the sorption systems. Tanashev et al. showed that the thermal conductivity of $CaCl_2$/silica gel KSK increased from $0.13\ W\ m^{-1}\ K^{-1}$ to $0.5\ W\ m^{-1}\ K^{-1}$ as absorbed water content increased from 0.1 g/g to 0.8 g/g [16]. Heat transfer enhancement can be also achieved by binding or synthesizing adsorbent on the surface of the adsorber bed [17,18] or by physically mixing sorbents with materials with higher thermal conductivity, such as metal powders or synthetic graphite [19]. Restuccia et al. observed that the thermal conductivity of zeolite with 40 wt% aluminum hydroxide, $0.43\ W\ m^{-1}\ K^{-1}$, was greater than the thermal conductivity of zeolite with 40 wt% graphite or 40 wt% PTFE (polytetrafluoroethylene), 0.36 and $0.25\ W\ m^{-1}\ K^{-1}$, respectively [19]. Wu et al. synthesized a silica gel – copper nanopowder composite by a sol-gel process and measured the thermal conductivity by the transient plane source (TPS) method. Wu et al. found that the copper nanopowder enhanced the thermal conductivity by 20% to $0.19\ W\ m^{-1}\ K^{-1}$ [20]. Effective thermal conductivity of unconsolidated adsorbent improved from $0.106\ W\ m^{-1}\ K^{-1}$ to $0.363\ W\ m^{-1}\ K^{-1}$ by adding 15 wt% shaved aluminum [21]. Kim et al. fabricated silica gel composite mixed with expanded graphite powders by compressive molding method. The thermal conductivity of the composite blocks is reported $10–20\ W\ m^{-1}\ K^{-1}$ depending on the graphite bulk density [22,23]. Sorption heat pumps with composite materials can have higher specific cooling power and lower investment cost [19].

The specific cooling performance (SCP) can be improved by the development of new composite materials with high water uptake and increased heat and mass transfer properties. In this study, $CaCl_2$-silica gel was selected for its known strong water sorption properties. Composites were prepared with organic binders (polyvinylpyrrolidone) and thermally conductive additives. The surface area and pore size distribution were measured. Water uptake and multi-cycle performance of the samples at different temperatures were measured and the thermal conductivity of the composite adsorbents and a mixture of silica gel and graphite flakes (0–20 wt%) studied under different controlled relative humidity.

2. Experimental study

2.1. Sample preparation

Composite sorbents were prepared utilizing chromatography-grade commercial silica gel (SiliaFlash® B60, Lot 011112, Silicycle, Inc., Quebec, Canada) with 0.2–0.5 mm irregularly shaped grains and average pore diameter of 6 nm. In batches of 50 g, the dry mesoporous silica gel was wetted with ethanol. An aqueous solution containing $CaCl_2$ and either 10,000 MW polyvinylpyrrolidone (PVP10) binder (Sigma Aldrich) or 40,000 MW polyvinylpyrrolidone (PVP40) binder (Amresco) was added, and the slurry was dried in a fume hood for 24 h. The damp materials were oven dried at 180 °C for over 2 h. The composition and volume of solution added to the silica gel was such that the consolidated composite produced was 28 wt% $CaCl_2$ and 15 wt% PVP. Dry silica gel in 4 g batches was combined with PVP (12–15 wt%) and thermally conductive graphite flakes (150 μm, Sigma-Aldrich) or copper powder (<425 μm, Sigma-Aldrich). The graphite flakes added to the composite included both fine particles and thin flakes up to 1.3 mm long, while the copper particles were small (up to 0.41 mm). Consolidated composites with thickness of 3.6 mm were also prepared with and without $CaCl_2$. The slurries were baked for one hour at 50 °C until damp or dry, and then heated to 180 °C for one hour. The sample names and compositions of the sorbent composites are given in Table 1.

2.2. Characterization

Nitrogen sorption isotherms of the samples were collected with a volumetric physisorption analyser (ASAP 2020, Micromeritics Instruments) to determine the specific surface area (S_{BET}), average pore diameter (D) and pore volume (V). Prior to testing, the samples were dried under vacuum at 150 °C for 1 h, followed by 2 h