



Hygroscopic salts in porous matrices: Thermophysical properties and lab-scale testing for air conditioning applications

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Abstract

This paper presents the preparation and testing of composite sorbents containing CaCl_2 , silica gel and binder in a lab-scale sorption chiller. The material properties of the composite sorbent are discussed with respect to the practical and operating cycle requirements. A fin and tube heat exchanger coated with 1.3 kg of sorbent was operated with 15, 30, 30 and 90 °C cycle conditions (evaporator, condenser, adsorption and desorption). The sorption chiller had a peak specific cooling power (SCP) of 245 ± 4 W/kg of sorbent and 78 ± 1 kW/m³ of sorber bed volume.

1. Introduction

Highly porous sorbents typically have low thermal conductivity, 0.1-0.2 W/(m·K), which combined with a high thermal contact resistance—at the interface with the heat exchanger in packed beds—significantly impedes the heat transfer and the performance of sorption-based thermal storage systems [1]. Enhancing mass and heat transport in sorbents is therefore important to improve the performance and market competitiveness of sorption heat transformers and thermal storage systems. Therefore, the dynamics of water vapor sorption have been investigated by pressure jump and temperature jump tests on small sorbent samples [2-4] and sorbent coated fins or small heat exchangers [5, 6]. Ammann et al. recently developed a serial heat and mass transfer impedance model and experimental methodology to quantify heat and mass transport limitations from water sorption dynamics and demonstrated that the sorption rate of small samples could be doubled by reducing thermal contact resistance or enhancing mass transfer [7, 8].

CaCl_2 -silica gel has been identified as one of the best water absorbents for air conditioning and heat pumping purposes [9, 10]. CaCl_2 is combined with silica gel because a mesoporous matrix is needed to contain the solution formed as the salt absorbs water vapor in order to avoid leakage of liquid sorbent from heat exchangers packed or coated with sorbent for sorption heat pumps and dehumidification systems. The optimal weight percent of salt added to the matrix depends of the pore volume needed to contain the solution that forms, which in turn depends on the operating cycle parameters.

Few lab-scale sorption cooling system tests have been performed with the water and CaCl_2 -silica gel working pair that is the focus of this study. Freni et al. tested a sorption chiller with an aluminum alloy finned tube heat exchanger coated with a compact layer of CaCl_2 in mesoporous silica gel consolidated with bentonite clay. The cooling coefficient of performance (COP) was 0.15 to 0.3 and the specific cooling power (SCP), 150-200 W/kg, was one order of magnitude higher than the same system run with granular bed of CaCl_2 in mesoporous silica gel (20 W/kg) [11]. Salt-in-mesoporous matrix sorber beds have been tested with other absorbents, e.g. ammonia and methanol [12], and other salts, such as calcium nitrate [13].

Wang et al. studied an ammonia- CaCl_2 adsorption ice making system, testing the absorbent with and without added expanded natural graphite [12]. The ice making system had an SCP of 140 W/kg, when run with pure CaCl_2 (thermal conductivity of 0.2 W/m·K), however, the SCP increased to 640 W/kg when the salt was mixed with 20 wt% expanded natural graphite and compressed into a consolidated composite with enhanced thermal conductivity of 7.2 W/m·K. The working pair tested in our system is different, water- CaCl_2 , however the evaluation of performance of ZnO and CaCl_2 coatings sets a baseline for future studies of coatings with enhanced thermal properties that are currently under development. In the present study, CaCl_2 in silica

gel sorbent consolidated with binder (PVA) is characterized and tested in a lab-scale sorption chiller.

2. Experimental methods

2.1. Composite preparation and characterization

To study the effect of matrix pore size on water sorption by CaCl_2 , the salt was deposited into commercial silica gels with irregular-shaped grains (0.2-0.5 mm) and average pore diameters of 4, 6, 9 and 15 nm (SilicaFLASH B40, B60, B90 and B150, Silicycle, Inc., Quebec, Canada). High resolution isotherms were measured using a thermogravimetric water vapor sorption analyzer (IGA-002, Hiden Isochema). The sorbent samples were also studied by transient plane source thermal constants analysis (TPS 2200, Thermtest) and nitrogen porosimetry (Quantachrome iQ-MP). Consolidated sorbents were prepared by the addition of polyvinyl alcohol (PVA) binder.

A commercially available heat exchanger (engine oil cooler #1268, Hayden Automotive) was filled with 1.3 kg of sorbent with a composition of 30% CaCl_2 , 55% silica gel (SilicaFLASH B150), and 15% PVA binder (Fig.1). The surface area, volume and weight of the finned tube heat exchanger (painted copper tubes, aluminum fins) were 2.8 m^2 , 4.1 L, and 2.54 kg. The aqueous salt and binder solution was added to silica gel to create a thick slurry that was pressed into the heat exchanger. After overnight oven drying at 80 °C and curing at 150 °C, more of the composite mix was pressed into the opposite side of the heat exchanger to fill voids, and the sorbent was again oven dried and cured. The sorbent was tested in our lab-scale chiller, described by Sharafian et al. [14] with upgrades to valves and piping. The lab-scale chiller (Fig. 2) has two sorber beds



Fig. 1: Heat exchanger loaded with CaCl_2 -silica gel and binder and closer view of the composite and heat exchanger fins (centre).

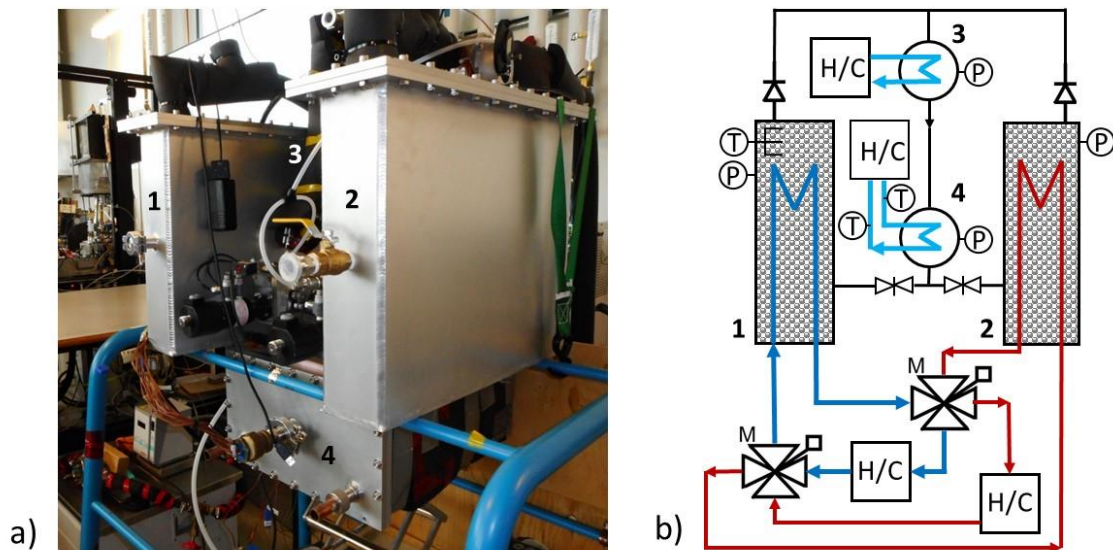


Fig. 2: Lab-scale sorption chiller a) photo and b) schematic showing two sorber beds (1,2), condenser (3), CALPE evaporator (4), valves, sensors and heating/cooling (H/C) circulators.

connected to two heating/cooling (H/C) circulators through two four-way valves for automated cycling from absorption to desorption temperatures. Two additional H/C circulators controlled the temperature of the condenser and custom-built capillary-assisted low-pressure evaporator (CALPE). Gate valves (50 mm) were used to control vapor flow from the evaporator and two sorber beds, while check valves (< 0.25 kPa cracking pressure) controlled vapor flow between the sorber bed and condenser. Three flowmeters, four pressure sensors, and twelve thermocouples were used to monitor the system.

The SCP and volumetric specific cooling power (VSCP) are calculated from the heat transfer measured at the evaporator, the full cycle time and the mass or volume of sorber bed as follows:

$$SCP = Q_{evap} / (m_{ads} \cdot t_{cycle}) \quad (1)$$

$$VSCP = Q_{evap} / (V_{ads} \cdot t_{cycle}) \quad (2)$$

where

$$Q_{evap} = \int_0^t \dot{m} c_p (T_{in} - T_{out}) dt \quad (3)$$

The reported SCP and VSCP values have an uncertainty of 11%, as described by Sharafian et al. [14].

3. Results

The thermal conductivity and specific heat of the composite, determined by transient plane source thermal analysis in a dry atmosphere, were 0.098 ± 0.002 W/m·K and 0.42 ± 0.06 MJ/m³·K, respectively. This is consistent with the results reported by Fayazmanesh et al. [15] and Aristov et al. [16]. Water sorption isotherms were collected on loose grain CaCl₂-silica gel composites prepared with silica gels with four different average pore diameters (4, 6, 9, 15 nm). The isotherms show the influence of the host matrix on the water uptake of the salt. The first inflection point in the curve marks the formation of the solid dihydrate. The second inflection occurs as the tetrahydrate becomes a hydrate melt within the mesopores and is followed by a region where the isotherm curvature is influenced by the silica gel pore size. An inflection in the adsorption curve and hysteresis in the desorption curve were observed to indicate when salt solution floods the mesopores and absorption by the salt solution continues in macropores and intergranular space at high partial pressure (P/P_0) (Fig. 3 a). It was determined that porosimetry data and the concentration dependent solution density can be used to calculate the partial pressure at which mesoporous matrix floods for a given matrix material and salt content.

The composition of the salt and host matrix was matched to sorption chiller operating cycle conditions such that the volume of the solution created by the salt and absorbed vapor would not exceed the available pore volume. When the CaCl₂ in silica gel was consolidated with a binder, vapor off-gassing during the curing

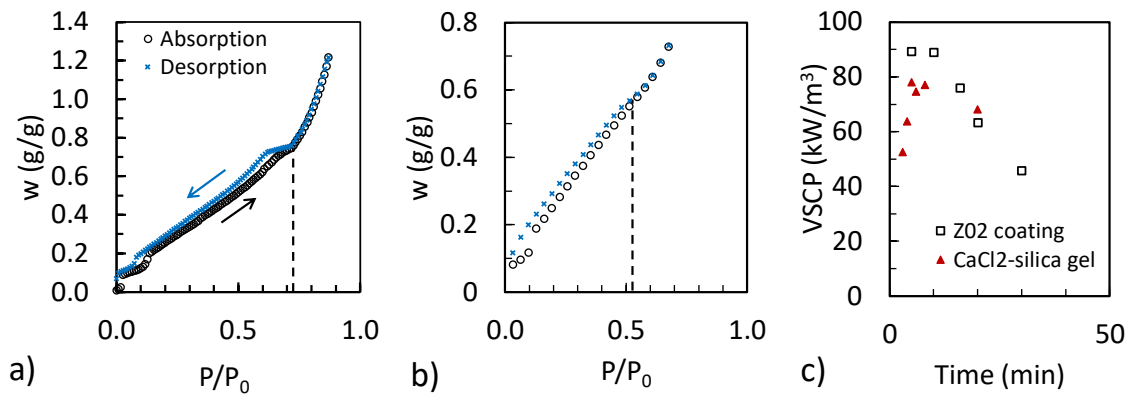


Fig.3: Water isotherms for a) loose grain CaCl₂ (28 wt%)-silica gel and b) CaCl₂-silica gel consolidated with 15% PVA. Dashed lines mark the partial pressure at which the salt solution has flooded the mesopores. c) Sorption chiller performance of the composite consolidated with 15% PVA as compared to a Z02 coating on an identical heat exchanger (0.3 mm, 0.8 kg).

process created intergranular porosity. While this improves mass transport, the drying and curing rates must be controlled to prevent the formation of larger and poorly bound pockets. Gas diffusivity through the intergranular space of the composites is currently being studied in our laboratory.

For the initial tests of the composite in our lab-scale sorption chiller, a large quantity of binder (15%) was used, which created a thin layer at the surface that may have affected mass transport and system performance. The isotherm for the composite and the SCP of our lab-scale chiller for evaporator, condenser, adsorption and desorption temperatures of 15, 30, 30 and 90 °C are shown in Fig. 3. The SCP for 5-minute cycles was 245 ± 4 W/kg or 78 ± 1 kW/m³. For comparison, the previously reported peak SCP of our sorption chiller for an identical heat exchanger coated with 0.3 mm of ASQOA FAM-Z02 by Mitsubishi Plastics was 456 W/kg or 90 kW/m³ [17].

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