EVALUATION OF $CaCl_2$-SILICA GEL SORBENT FOR WATER SORPTION COOLING SYSTEMS

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Abstract

Hygroscopic salts supported by a mesoporous matrix for improved mass transport are promising sorbents for water-based sorption cycles that operate at low pressure. In this study, loose grain composites of $CaCl_2$ supported by mesoporous silica gels with four distinct pore size distributions were prepared and compared with AQSOA FAM-Z02, a silicoalumuninophospate zeolite desiccant. A salt silica sorbent consolidated with graphite flakes and binder was also analyzed. The sorbents were evaluated with a volumetric nitrogen physisorptionporosimeter and thermogravimetric water vapor sorption analyzer. The hygroscopic salt filled 56–60 % of the open pore volume of the mesoporous silica gel supports. Water uptake capacity of the $CaCl_2$/silica gel sorbent was up to 0.33 g per gram of dry sorbent at 12 mbar and 35˚C, and sample performance was consistent through 200 wetting-drying cycles.

KEYWORDS

Calcium chloride, sorption cooling, water isotherm

INTRODUCTION

The vapor compression systems commonly used for air conditioning and refrigeration consume significant amounts of electrical power and employ environmentally harmful refrigerants. The power used by HVAC systems to provide thermal comfort in residential and commercial buildings amounts to 10–20% of the total energy consumed in the developed world [1–3]. Efficient, sustainable cooling technologies are presently the focus of significant research and development efforts. In adsorption cooling systems, evaporative cooling power is created as aporous sorbent material, which can be regenerated with thermal energy, adsorbs or absorbs a refrigerant, such as water.

Sorption cooling systems that utilize materials with low regeneration temperatures can be powered by low-grade heat sources, including solar thermal and industrial waste heat [4].The selection of an effective sorbate-sorbent working pair for a specific adsorption system depends on the intended operating conditions, particularly the temperatures and working pressures for adsorption and desorption. Zheng et al. [5] and Aristov [6] reviewed solid desiccants for sorption cooling systems andcompared salt in a host matrix composites with other the classes of sorbents, including silica gels, zeolites, aluminophosphates, porous polymeric metal-organic frameworks, and porous carbons.Both reviews conclude that salt in porous matrix sorbents are strong candidate materials with properties that can be tuned through selection of the host material and the salt.

The focus of this research is the preparation and evaluation of sorbent materials for water sorption systems with a target regeneration temperature of 80˚C, particularly $CaCl_2$-silica gel sorbents. This sorbent type was chosen for its uptake capacity and uptake rate under the desired operating conditions. Glaznev et al. compared SWS-1L, a $CaCl_2$ in SBA-15 silicate composite with microporous silica and AQSOA FAM-Z02silicoalumuninophospate by the large-temperature jump method and determined it had a superior instantaneous specific cooling power[7]. The sorbent choice is also motivated by the availability of affordable salts and silica gels, and the ease of synthesis of batches ranging from grams of material for characterization to kilograms of material for testing in a lab-scale sorption chiller.

Water-based sorption chillers operate at low pressures and sorption dynamics have proven to be very sensitive to the presence of even a fraction of a millibar of background gas, as was demonstrated by Glasnev et al. in tests of silica gel, $CaCl_2$ in silica gel and Z02 [8]. Sorbents containing $CaCl_2$can contribute to the corrosion of metal heat exchangers, particularly mixed metal heat exchangers susceptible to galvanic corrosion. In our lab-scale sorption chiller tests, we observed performance loss due gas released by the corrosion of a copper-aluminumsorber bed heat exchanger after a single desorption cycle and the restoration of performance with the evacuation of this background gas between cycles. However, a sorption chiller with $CaCl_2$ in mesoporous silica gel coated on an aluminum alloy heat exchanger was run for 100 cycles by Freni et al. without any trace of corrosion or performance loss [9].

For loose grain sorbent-heat exchanger designs, sorption kinetics studies have revealed that for grain sizes below 0.5–0.8 mm the kinetic curves do not change appreciably, for example, one layer of 0.8 mm silica gel grains can deliver the same specific cooling power as four layers of 0.2 mm grains[10–12]. The sorption rate depends on the transport of water vapor in the porous matrix and the dissipation of the heat of adsorption. In the case of salt in silica gel composites, absorption of water vapor by the salt dispersed in the porous matrix creates a solid hydrate, and then an aqueous solution [13]. The solution formation complicates sorption kinetics compared to water sorbed by silica gel or zeolite surfaces.

The salt confined in the support matrix undergoes water absorption, dissolution and dilution. The density of the solution depends on the temperature and the mass fraction of $CaCl_2$.The enthalpy of adsorption is also concentration dependent. Condereviewed the properties of aqueous solutions of $CaCl_2$ and LiCl to generate and validate equations for the solubility boundary, vapor pressure, surface tension, dynamic viscosity, thermal conductivity, specific thermal capacity, density and differential enthalpy of dilution [14].

There is a pore filling threshold where the salt solution leaks from the pores and forms a film on the surface of the silica particles. Tanashev et al. measured the change in the thermal conductivity of salt in silica composites as a function of adsorbed water and observed a steep rise when the salt solution leaked from the pores, connecting the silica gel particles and enhancing heat transfer [15]. They found that for $CaCl_2$ and the other salts tested a steep increase of thermal conductivity occurred when the calculated volume fraction of the pores occupied with salt solution was 0.60-0.64. As salt solution leakage is detrimental to performance sorption chillier performance, systems should be designed to avoid this regime of operation [16].

This paper presents porosimetry and water sorption measurements of $CaCl_2$ confined in silica gels with mean pore diameters ranging from 4 to 16 nm. The results are compared to the water uptake properties of commercial sorbent material AQSOA FAM-Z02.

EXPERIMENTAL

Chromatography-grade commercial silica gels with four distinct pore size distributions and 0.2–0.5 mm irregular-shaped grains were acquired from Silicycle, Inc. (Quebec, Canada). Concentrated salt solutions were prepared with oven dried $CaCl_2$ (Fisher Scientific). The silica gels, in 100 g of 500 g batches, were wetted with ethanol, and then aqueous $CaCl_2$ solution was added to the silica such that complete deposition of the salt into the mesoporous silica would produce the desired product. The mixtures dried for 24 hours in a fumehood, and 500 g batches were further warmed on a hot plate to accelerate drying. The damp material was baked at 200 °C until judged dry by consistent successive weight measurements. The mesoporous silica, SiliaFlash types B40, B60, B90 and B150, will be referred to hereafter as S4, S6, S9 and S15, while the silica supported salt composites will be referred to as $CaCl_2$-S4, $CaCl_2$-S6, $CaCl_2$-S9 and $CaCl_2$-S15. The composites were 28 wt% $CaCl_2$with the exception of $CaCl_2$-S4 (30 wt%).

Salt in silica gel samples consolidated with organic binder polyvinyl pyrrolidone (PVP) (40,000 MW, Sigma Aldrich) and graphite flake(+100 mesh, <150 μm, Sigma Aldrich),as a thermally conductive additive, were prepared in small batches. The components were combined in an aqueous solution that was dried on a hotplate, and then heated to 180 °C to cross-link the polymer. The product, $CaCl_2$-S15G, was 30% $CaCl_2$, 30% silica, 15% PVP and 25% graphite flake by weight.Silicoalumuninophospate desiccant AQSOA FAM-Z02 was acquired fromMitsubishi Plastics. This zeolite, referred to hereafter as Z02, was in the form of 1.8–2 mm diameter pellets containing 6–17 wt% silicon dioxide binder.

Nitrogen isotherms at 77 K were collected with a volumetric gas adsorption analyzer, (ASAP 2020, Micromeritics Instrument Corp., USA) to determine the textural characteristics of the silica gels and composites. The samples were degased under vacuum at 150 °C for one hour, followed by two hours at 200 °C prior to the measurements. The Brunauer, Emmett and Teller (BET) model was used to calculate the specific surface area, S_{BET} [17]. Incremental pore volume per pore width distributions were calculated from the adsorption branch of the isotherm using the Barrett, Joyner and Halenda (BJH) model [18].

Water sorption isotherms were collected with a thermogravimetric analyzer (TGA) (IGA-002, Hiden Isochema, UK). The samples were dried under vacuum at 200 °C for six hours to determine their dry weight. Multiple isotherms were collected for each sample without repeating the drying process. That is, each isotherm ended with a final desorption, outgassing step at the isotherm temperature, and the next isotherm began after the automated system adjusted the sample temperature. The kinetic data for each pressure step were analyzed by a real time processor and successive pressure steps were taken when water sorption was 98.5% of the predicted equilibrium. The water uptake was calculated either as

$$w\left(g_{H_2O}/g_{sorbent}\right)=m/m_{dry} \quad \text{or} \quad N\left(mole_{H_2O}/mole_{CaCl_2}\right)=\frac{m/M_{H_2O}}{\left(m_{dry}\cdot C\right)/M_{CaCl_2}},$$

where the molar masses, M, of H_2O and $CaCl_2$ are 18.15 g/mol and 110.98 g/mol, respectively, and C is the wt% of salt in the composite. Short term durability studies of the $CaCl_2$ – S15 composite were conducted with the TGA through 200 pressure swing cycles at 35 °C, whereby the sample was exposed to alternating 12 mbar H_2O and vacuum outgassing conditions.

RESULTS

The N_2 adsorption/desorption isotherms of the silica gels and $CaCl_2$/silica composites were Type IV with H1 hysteresis loops, typical of mesoporous materials. The isotherms for the $CaCl_2$ – S4 and $CaCl_2$ – S15 composites and their pure silica gel supports are shown in Fig. 1, and the calculated textural characteristics are summarized in Table 1. Consistent with previous reports, the results indicate that CaCl2 fills the silica gel pores and decreases the specific surface area and pore volume. The high uncertainty in pore size distributions calculated from the adsorption branch of N_2 isotherms by the BJH method has been recently discussed by De Lange et al. [19]. The incremental pore volume per pore width curves in Fig. 1 provide a qualitative indication of the change in the pore size distribution of $CaCl_2$ – B6 relative to B6, specifically the decrease in pore volume and change in the pore size distribution due to the preferential filling of small pores. The qualitative relative differences in the pore sizes distributions of the different silica gel salt composites prepared for this study are also shown. $CaCl_2$ – S4 and $CaCl_2$ – S15, the samples with the greatest difference in pore size distribution, were selected for detailed comparison of their water sorption characteristics.

Table 1. Textural characteristics of samples calculated from N_2 adsorption isotherms

No.	S_{BET} (m^2 g^{-1})	Pore vol. (cm^3 g^{-1})	Mean pore diam.(nm)	No.	S_{BET} (m^2 g^{-1})	Pore vol. (cm^3 g^{-1})	Mean pore diameter (nm)
S4	574± 2	0.58	4	$CaCl_2$-S4	146.7 ± 0.5	0.27	7
S6	487 ± 2	0.75	6	$CaCl_2$-S6	134.5 ± 0.4	0.37	9
S9	406 ± 0.4	0.83	8	$CaCl_2$-S9	148.3 ± 0.4	0.58	10
S15	276 ± 0.8	1.10	16	$CaCl_2$-S15	136.3 ± 0.4	0.60	18

The water adsorption branch of the complex isotherms of $CaCl_2$ – S4 and $CaCl_2$ – S15 collected at temperatures from 25 to 80 °C are shown in Fig. 2. The initial transition from $CaCl_2$ to $CaCl_2{\cdot}2H_2O$ (~10 wt%), is most clearly shown in the 50 °C and 80 °C curves, occurring near 2 mbar and 11 mbar, respectively. The transition is steeper for $CaCl_2$ – S15 compared to $CaCl_2$ – S4, as is the next increase in curvature occurring at ~ 12 mbar on both of the 50 °C curves. This distinctive difference between the adsorption of $CaCl_2$ in S4 versus S15 is seen more completely in the 35 °C curves, as a bulge on the $CaCl_2$ – S4 isotherm from 4–14 mbar. The equivalent features are subtler in the $CaCl_2$ – S15 isotherm, but the end of this region is visible as a single point divot at 10.1 and 12.6 mbar in the 25 °C and 35 °C curves, respectively. This difference is further illustrated by the plots of N (mole H_2O per mole $CaCl_2$) as a function of relative pressure, P/P_0, for $CaCl_2$ – S4 and $CaCl_2$ – S15 at 25 °C are shown in Fig. 2c. When plotted as a function of relative pressure, P/P_0, the isotherms collected at different temperatures were parallel with slightly lower sorption capacity with increasing temperature. The offset reflects the strong $CaCl_2$-water interactions, however, we have not yet ruled out the possibility of a contribution from instrumental systematic error, such asan imperfect buoyancy correction.The complex shape of thesorption-desorption isotherm to ~ 0.9 P/P_0 at 35 °C for $CaCl_2$ – S15 is shown in Fig. 2d.

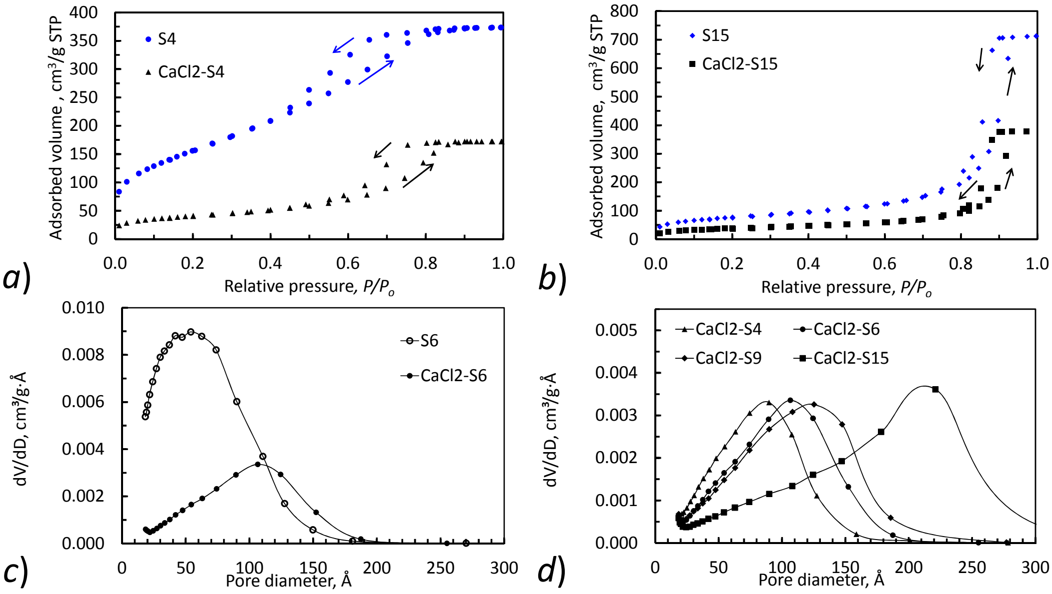

Fig. 1 Comparison of the N2 isotherms for a) S4 and CaCl2 – S4, and b) S15 and CaCl2 – S15. Comparison of qualitative incremental pore volume per pore width for c) S4 and CaCl2 – S4, and d) CaCl2 supported by different silica gels

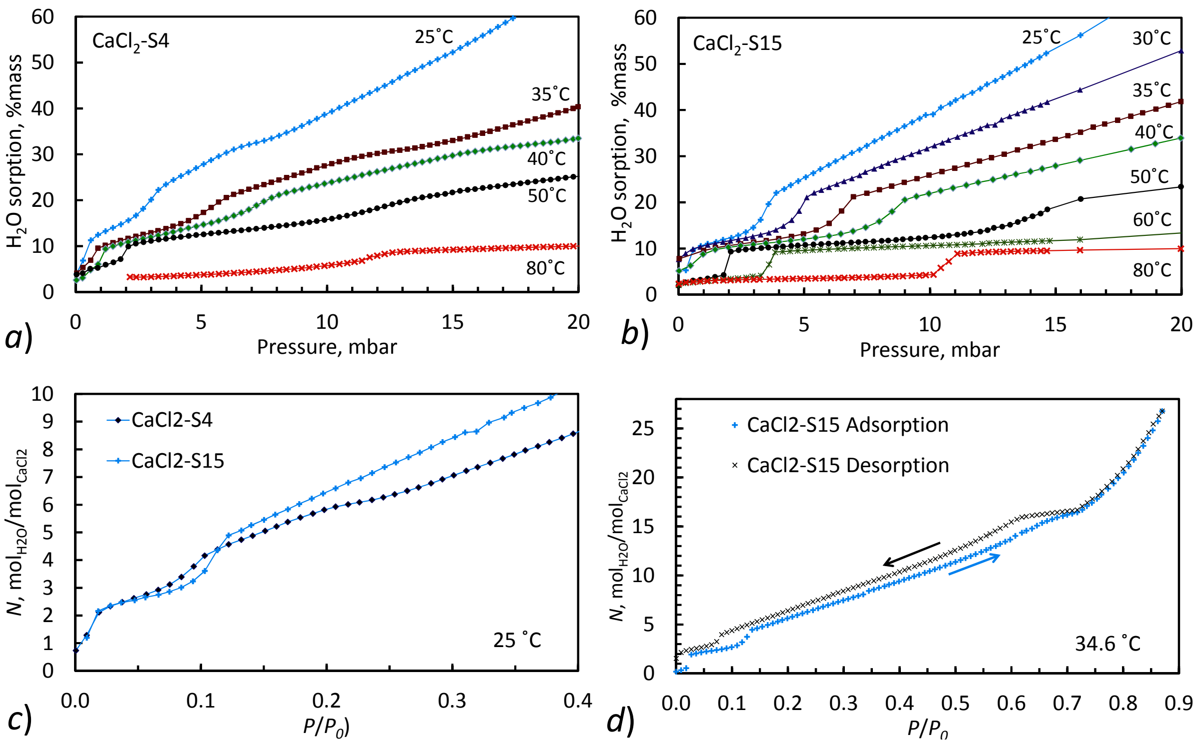

Fig. 2. Water sorption isotherms from 25 to 80 °C for a) $CaCl_2$ – S4 and b) $CaCl_2$ – S15. c) Water sorption of isotherms of $CaCl_2$ in S4 and S15 in mole H_2O per mole $CaCl_2$ at 25 °C. d) Water sorption isotherm of $CaCl_2$ – S15 to high partial pressure at 35 °C

As the salt absorbs water, it transforms into solid $CaCl_2 \cdot 2H_2O$, and then deliquesces. The bulk melting point of $CaCl_2 \cdot 4H_2O$ is 45 °C [20], however the melting point of salt confined in silica is known to be depressed. Following the equations of Conde [14], the density of aqueous $CaCl_2$ solutions can be calculated as a function of the mole fraction of the salt relative to the water. In Fig. 3, the weight of water adsorbed as a function of pressure and the weight of salt in the composite are used to estimate the volume of solution in the composite at various vapor pressures. However, the capillary forces between the solution and porous matrix are known to affect the solution density. On each curve, the vapor pressure at which the upper closure of the hysteresis loop occurs in the water sorption isotherms is marked. At this point, the pores are filled with solution, and the change of curvature of the isotherm above this point reflects the transition to sorption into the salt solution that has leaked into the interparticle space between the silica gel grains (Fig. 2d). The upper closure point of the hysteresis loops for $CaCl_2$ – S4 and $CaCl_2$ – S15occurred at 16 mbar and 40 mbar H_2O, respectively, when the calculated volume fraction filled wasonly 0.8 and 0.74.

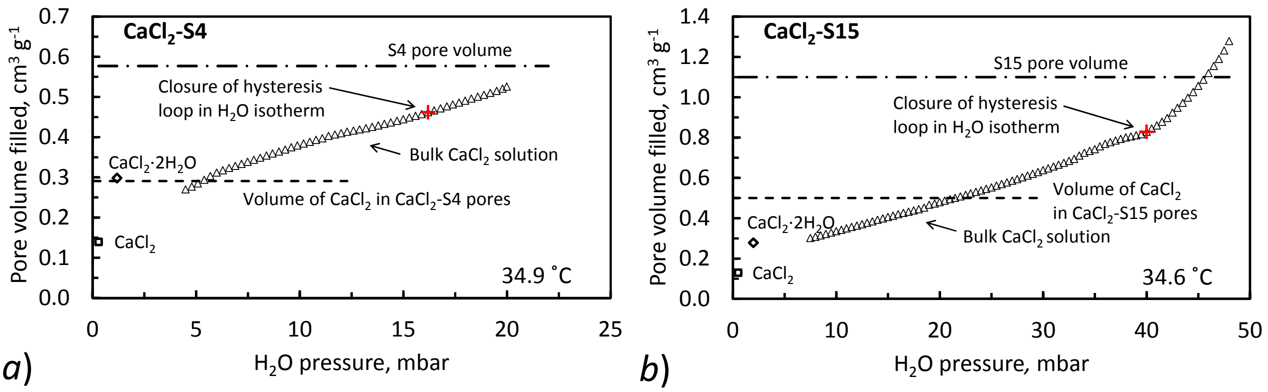

Fig. 3. Comparison of measured pore volume for a) S4 and $CaCl_2$ – S4 and b) S15 and $CaCl_2$ – S15 from N_2 isotherms with H_2O isotherm "pores filled" point (✚), and calculated volume of $CaCl_2$ (□), $CaCl_2$ – $2H_2O$ (◇)and $CaCl_2$ solution (Δ) calculated from the mass of sorbed water as a function of pressure and associated $CaCl_2$ molar fraction

The upper dashed lines in the plots in Fig. 3 show the pore volume of silica gel host matrices, S4 and S15, and the lower dashed lines indicate the measured fraction of that pore volume filled by $CaCl_2$ in the salt-silica composites. Both these values were determined by nitrogen porosimetry. It is shown that the volume filled by salt far exceeds the volume calculated from the weight of $CaCl_2$ and its bulk density, 2.15 g cm^{-3}. The measured volume filled by dry $CaCl_2$ suggests that the density of the deposited $CaCl_2$ is low, even comparable to the density of concentrated aqueous $CaCl_2$ solutions. Alternatively, $CaCl_2$ could be blocking but not filling some of the pores, resulting in the lower pore volume of the composite.

The water sorption, pressure and temperature for 12 mbar pressure swing tests of $CaCl_2$ – S15G and Z02 are shown in Fig. 4. During tests, a water bath at 35 °C surrounds the reactor cylinder and the temperature readings are from a thermometer directly adjacent to the sample. From these curves, near equivalent specific cooling powers for cycles to 80% of the sorption capacity, $\Delta w_{0.8}$, were calculated as $W_{0.8} = \Delta w_{0.8} \cdot \Delta H_{vap} / \tau_{0.8}$ where $\tau_{0.8}$ is the uptake time and ΔH_{vap} is the heat of vaporization of water, 2478 kJ/kg). Under these test conditions, the specific cooling power of $CaCl_2$ – S15G, containing 25 wt% graphite flakes and 15 wt% binder, was 0.54 kW/kg compared to 0.60 kW/kg for the benchmark material, Z02. The sorption performance of $CaCl_2$ – S15 was tested for 200, 20 min pressure swing cycles at 35 °C and found to be consistent with and initial and final $\Delta w_{\mathrm{cycle}}$ of 0.196 and 0.195 g/g. Review of the detailed data indicated that the both the adsorption step final weight and desorption step final weight increased slightly during the 200 cycle run, the difference in these increases created the 0.001 drop in $\Delta w_{\mathrm{cycle}}$. The water sorption isobars for $CaCl_2$ – S15 and Z02 are presented in Fig. 5 along with the equilibrium adsorption times for 0–12 mbar pressure swings at each temperature. It is of note that the uptake rate for Z02 declines significantly at ~ 40 °C, ahead of the temperature where there is a sharp drop in uptake capacity.

Table 2. Uptake, time, and power for pressure swing cycles (0-12 mbar) for 80% equilibrium sorption capacity

Sample	T (˚C)	Dry wt (mg)	w_{initial} (g/g)	w_{final} (g/g)	$\Delta w_{0.8}$ (g/g)	$\tau_{0.8}$ (min)	$W_{0.8}$ (kW/kg)
$CaCl_2$-S15G	35	21.231	0.038	0.241	0.163	13.0	0.54
Z02	35	19.358	0.036	0.274	0.190	12.5	0.60

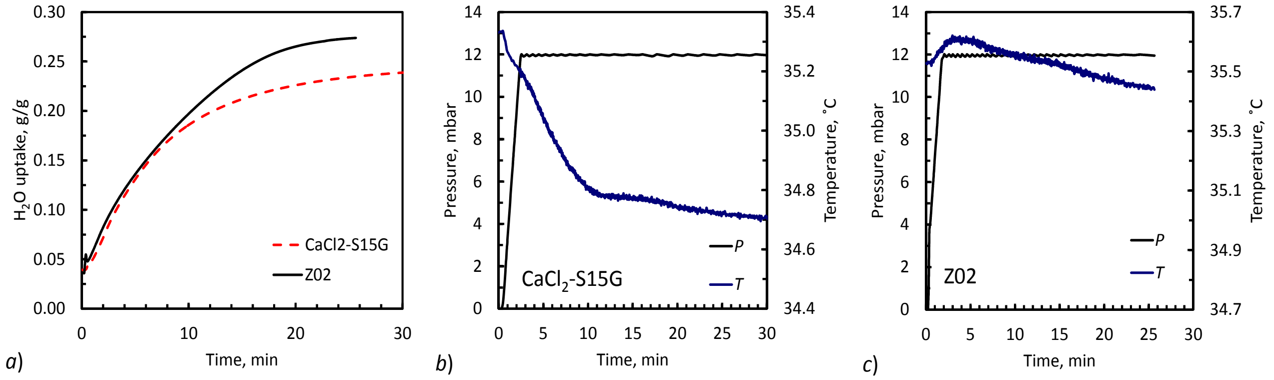

Fig. 4. *a*) Water sorption as a function of time for a 12 mbar pressure swing for Z02 and $CaCl_2$ – S15G (g/g total weight of composite). Test pressure and temperature conditions for *b*) $CaCl_2$ – S15G and *c*) Z02

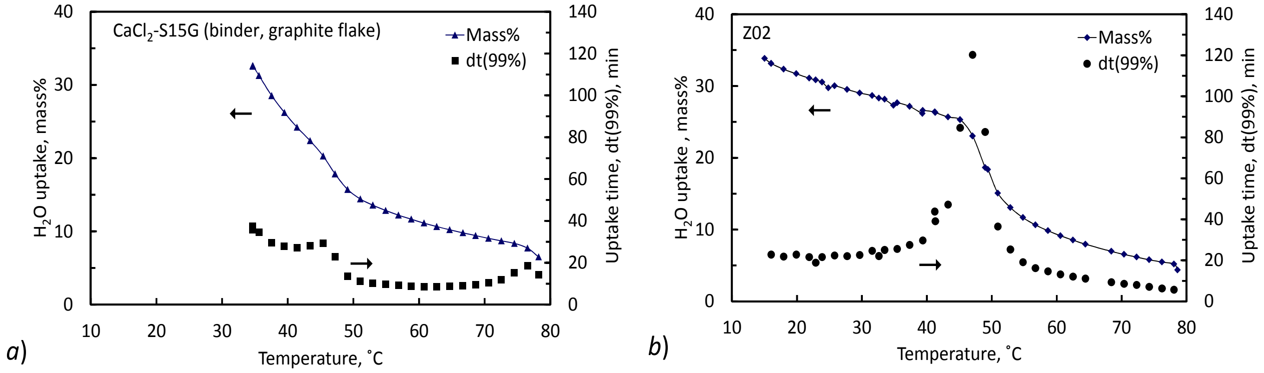

Fig. 5. Water sorption isobars at 12 mbar and the equilibrium adsorption time (dt 99%) for 0–12 mbar pressure swings at each temperature for a) $CaCl_2$ – S15G (mass % based on the dry weight of sorbing ingredients, $CaCl_2$, S15 and binder with the graphite flake weight excluded) and forb) ASQOA FAM-Z02 pellets

The water sorption isosters for $CaCl_2$ – S15 and Z02 are plotted in the ln(P_{H2O}) versus 1/T form in Fig. 6 for various amounts of sorbed water, *w* (g/g).

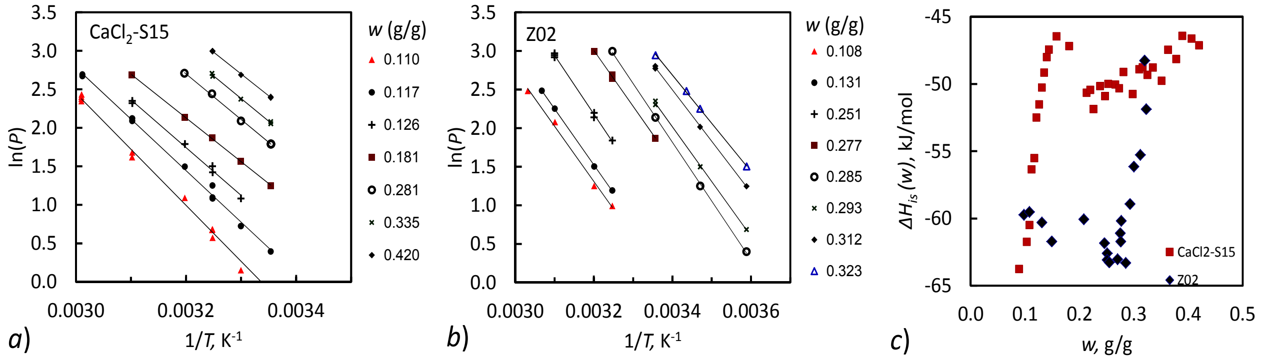

Fig. 6. Isosters for *a*) $CaCl_2$ – S15 and *b*) Z02 and *c*) isosteric water sorption heat for $CaCl_2$ – S15 and Z02

The isosteric heat of water sorption is determined as a function of the slope of the linear isosters, where $\ln(P) = B(w)/T + C(w)$ and $\Delta H_{is}(w) = B(w)R$ and R is the universal gas constant. The increase in $\Delta H_{is}(w)$ to –63.7 kJ/mol as w approaches 0.09 (N = 2) is due to the formation of solid hydrates with more strongly bound water molecules, and is consistent with reports from Aristov et al. (62.3 kJ/mol isosteric desorption) for $CaCl_2$ in mesoporous silica gel [21].

CONCLUSIONS

Water sorbent composites of $CaCl_2$ supported by mesoporous silica gels were prepared and characterized. The water isotherms of $CaCl_2$ in silica gels with 4 nm and 16 nm average pore sizes were compared. The pore volume filled by solid $CaCl_2$ and concentrated aqueous $CaCl_2$ was measured and calculated for use in future diffusivity calculations through analysis small pressure step isotherms. Water uptake capacity of the $CaCl_2$/silica gel sorbent was up to 0.33 g per gram of dry sorbent at 12 mbar and 35 °C, and sample performance was consistent through 200 wetting-drying cycles. The isobars, isosters and isosteric enthalpy of water sorption of $CaCl_2$ – S15 and silicoalumuninophospate desiccant, Z02 were measured and compared.

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