



Further improvement of the synthesis of silica gel and CaCl₂ composites: Enhancement of energy storage density and stability over cycles for solar heat storage coupled with space heating applications[☆]



Emilie Courbon^{a,*}, Pierre D'Ans^b, Anastasia Permyakova^c, Oleksandr Skrylnyk^a,
Nathalie Steunou^c, Marc Degrez^b, Marc Frère^a

^a Department of Thermodynamics and Mathematical Physics, Université de Mons, 31 Boulevard Dolez, B-7000 Mons, Belgium

^b AMAT Department, Université libre de Bruxelles (ULB), 50 Avenue F.D. Roosevelt – CP 194/3, B-1050 Bruxelles, Belgium

^c Institut Lavoisier, Université de Versailles-Saint-Quentin-en-Yvelines, Université Paris Saclay, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France

ARTICLE INFO

Keywords:

Thermochemical storage
Composite
CaCl₂
Silica gel

ABSTRACT

Composite materials based on a silica gel loaded with CaCl₂ are of great interest for seasonal thermochemical heat storage. In order to improve the performance of these materials for this application, and to evaluate their multi-cycle stability, a new synthesis protocol is proposed, based on successive impregnation/drying steps by using a matrix with a broad pore size distribution. Through this method, a CaCl₂ content of 43 wt%, a high cycle loading lift of 0.40 g/g and an unprecedented energy storage density for this type of material of 211 kW h/m³ of packed bed composite, in conditions of a solar heat storage system (adsorption at 30 °C, desorption at 80 °C, and water vapor pressure of 12.5 mbar) can be reached. Moreover, the distribution of the salt inside the pores and the absence of any salt crust outside the matrix prevent salt leakage, leading to an outstanding preservation of the cycle loading lift after 10 cycles. Based on Polanyi theory, it can be assumed that the energy storage density can exceed 350 kW h/m³ for water sorption at 20 °C, desorption at 80 °C, with both steps at a water vapor pressure of 12.5 mbar.

1. Introduction

Promoting the use of renewable energy sources is one of today's main challenges. Solar energy is one of the most promising options thanks to its high availability and low cost. To solve the problem of the discrepancy between the availability of solar heat and space heating needs, long-term storage systems have to be developed. Long-term heat storage systems need some specific requirements. For example, the storage material will be submitted to one charging phase and one discharging phase per year. As the system should be used for at least 20 or 25 years, the storage material should keep the same performance over at least 20–25 cycles. The long-term heat storage should be able to produce enough energy (e.g. 3000 kW h/year for a single-family house in Belgium) to cover the heat demand of a building, and so the material's energy storage density should be as high as possible to reduce the volume of storage needed to cover the heat demand of the building. Thermochemical heat storage, using a reversible sorption/desorption reaction, is the most promising solution due to the high energy storage density of thermochemical storage materials (up to 780 kW h/m³)

(Aydin et al., 2015; N'Tsoukpoe et al., 2014, 2009). Water has often been chosen as a sorbate due to its nontoxicity and low cost; that is why, in this paper, this is the only sorbate considered. A wide range of thermochemical storage materials have been discussed including salt hydrates (MgSO₄ (Ferchaud et al., 2014, 2013, 2012; van Essen et al., 2009b), CaCl₂ (Mugnier and Goetz, 2001; van Essen et al., 2009a), Li₂SO₄ (Ferchaud et al., 2013, 2012), CuSO₄ (Ferchaud et al., 2012; van Essen et al., 2009a), MgCl₂ (Ferchaud et al., 2013; Mugnier and Goetz, 2001; van Essen et al., 2009a; Zondag et al., 2013), Na₂S (Mugnier and Goetz, 2001), LiCl (Mugnier and Goetz, 2001) and SrBr₂ (Fopah Lele et al., 2015; Hennaut et al., 2014; Lahmidi et al., 2006; Michel et al., 2014, 2012)), physical adsorbents (such as activated carbons, silica gels, zeolites, metal organic frameworks (Elsayed et al., 2016; Permyakova et al., 2017)) and composite materials (salt encapsulated in a porous matrix). Among these materials, salt hydrates have the highest energy storage densities (several hundreds of kW h/m³) (Trausel et al., 2014). However, for some of these salts, their high water content in the conditions of thermal heat storage systems may cause their dissociation in solution and/or provoke morphological instability

[☆] SoTherCo Project: www.Sotherco.eu.

* Corresponding author.

E-mail address: Emilie.courbon@umons.ac.be (E. Courbon).

or aggregation of particles, which make their use in a thermochemical storage reactor difficult (Bouché et al., 2016; De Jong et al., 2014; Donkers et al., 2016; Solé et al., 2012; Whiting et al., 2014). Hence, composite materials have been developed with the aim of stabilizing the salt while keeping a high energy storage density, thereby limiting the volume of the storage system to be installed in the building architecture.

Among the salt hydrate candidates, calcium chloride is an interesting candidate for thermal heat storage thanks to its large availability, low cost and hydration rate of 5 mol of water per mole of CaCl_2 under thermochemical storage for space heating conditions. However, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is prone to transform spontaneously into a solution, which makes the use of CaCl_2 as pure salt in a thermochemical reactor difficult.

To solve the problem of the instability of pure CaCl_2 , a lot of research has been devoted to the development of efficient composites based on CaCl_2 . The incorporation of CaCl_2 into the pores of silica gel using a wet impregnation protocol with a large quantity of salt solution followed by filtration and drying steps, with possibly an additional washing step, has already been described (Aristov et al., 2002, 1996b). The influence of physical-chemical parameters on the salt content and on sorption properties was studied (Aristov et al., 1997, 1996a; Gordeeva et al., 2006; Tokarev and Aristov, 1997; Wu et al., 2007; Zhu et al., 2006). It was shown that salt content is closely dependent on both the pore size of the matrix (Zheng et al., 2014) and the salt concentration during the impregnation step (Elsayed et al., 2016), while the sorption capacity of composites is strongly linked to the salt content (Gordeeva et al., 2006; Wu et al., 2007; Zhu et al., 2006).

Interesting sorption properties were obtained for composites based on MCM-41 and CaCl_2 at 37.7 wt%, with a water sorption capacity and energy storage capacity at $p/p_s = 0.7$ of 0.7 g/g and 580 W h/kg respectively (Tokarev et al., 2002), and also for a silica gel/ CaCl_2 composite with a salt content of 30 wt% with a sorption capacity and energy storage capacity at 25 °C and 80% RH of 1.2 g/g and 940 W h/kg respectively (Gordeeva et al., 1999; Tohidi et al., 2009). A composite SBA-15/ CaCl_2 with a salt content of 43 wt% adsorbed 0.47 g/g at 50 °C and 37 mbar (Ponomarenko et al., 2010). In those studies, the water vapor pressure chosen for the adsorption step is high compared to real working conditions. Besides, the energy storage capacity is calculated assuming the composite is completely dry after the desorption step, which is not always the case depending on the heat source temperature.

Concerning seasonal heat storage applications, some composites based on CaCl_2 have already been studied in lab scale prototypes. A silica gel/ CaCl_2 composite with a salt content of 35 wt% (Zhu et al., 2006), which can adsorb 0.73 g/g at 30 °C and 80% RH, was tested in an open system. The water vapor pressure is particularly high in comparison to that used in heat storage systems (solar space heating). The performance of this composite was stable for 500 cycles, with a heat storage capacity of 264 W h/kg (no indication was given concerning the bed density to calculate the energy storage density). Ristić et al. (2012) developed a composite based on CaCl_2 and on sorbent FeKIL2 with a salt content of 7 wt%. The cycle loading lift, between the adsorption step at 25 °C and 12 mbar, and desorption step at 150 °C and 56 mbar, was 0.2 g/g, which corresponds to a heat storage capacity of 155 W h/kg (no indication concerning the bed density was given) with 3.6% loss of water uptake after 20 cycles between 40 °C and 150 °C at 56 mbar. The highest energy storage density was reported for a composite based on aluminosilicate and CaCl_2 in an open system: 180 kW h/m³ between 20 °C and 150 °C at 7.8 mbar (Jabbari-Hichri et al., 2015). These conditions were different from the reference conditions for solar thermal energy storage and space heating applications. The desorption temperature of 150 °C is quite high for thermal solar collectors, for which temperatures lower than 100 °C are typically used. In solar heat storage applications, the main challenge is to reach high energy storage density with a low temperature heat source for desorption (< 100 °C). Moreover, the adsorption temperature of 20 °C is too low for space heating

applications as it corresponds to the target comfort temperature of the room.

Despite the fact that numerous studies have been focused on CaCl_2 based composites, it is not always possible to evaluate their potential as thermochemical storage materials for solar thermal energy storage for space heating applications. The main reason for this is the lack of information about the energy density that can be reached – high energy storage density is required to limit the volume of the system – in conditions close to the application ones. The water uptake is not always measured in an adequate range of temperature and pressure for this application. The composite packing density is rarely provided, preventing the determination of the energy storage density.

Moreover, the stability over successive cycles is still the main issue (Ji et al., 2007), as the salt becomes liquid in the pores past a certain point of high water uptake, and problems of salt solution leakage from the matrix pores were reported, leading to a loss of performance after several cycles. For a good multi-cycle stability, the salt content of the composite should be limited and not exceed around 30 wt% (Wu et al., 2007), which also limits the sorption capacity and hence the energy storage density. For space heating applications, the energy storage density should be at least 150 kW h/m³, which represents a 20 m³ storage to cover the needs of a passive house. With this low salt content, this value of energy storage density would not be reached. Therefore, further improvements to the synthesis protocol are required in order to increase both the salt content of the composite and the energy storage density as well as enhancing the multi-cycle stability, which is of primary importance for seasonal heat storage for space heating applications.

When composites present high salt contents (Ponomarenko et al., 2010; Tokarev et al., 2002; Tokarev and Aristov, 1997), the location of the salt (on the surface of the matrix or in the pores) and the stability of composites have not been previously investigated. Concerning the target value of the energy density, one can refer to the most promising results that have been published so far when considering other salts than CaCl_2 , for example, zeolite 13X/ MgSO_4 (Hongois et al., 2011), silica gel/ $\text{Ba}(\text{OH})_2$ and silica gel/ LiNO_3 (Jabbari-Hichri et al., 2015). The best results were reported for the composite zeolite 13X/ MgSO_4 with an energy storage density of 166 kW h/m³ (desorption temperature of 150 °C, adsorption at 30 °C and 17–19 mbar) (Hongois et al., 2011). This composite required a high desorption temperature, which is too high for using thermal solar collectors (loss of efficiency of the collectors).

In this work, a composite based on silica gel and on CaCl_2 , synthesized with a different protocol than those previously reported, will be presented. The objectives are to optimize the salt content of the composite, its energy storage density, and multi-cycle stability. The energy storage density of the composite will be determined in conditions of a solar heat storage system coupled with space heating. The complete structural and chemical characterization of this composite will be performed in order to understand the mechanism of sorption and evaluate its stability.

2. Materials, synthesis and characterization

2.1. Materials

The silica gel used as a porous matrix in this study is Davisil grade 62 from Grace, hereafter called SG62. This silica gel has a broad pore size distribution, mainly with mesopores. The anhydrous calcium chloride (Caso® granules) with 94% purity was provided by Solvay.

2.2. Synthesis protocol

A few grams of composite were synthesized using the following protocol: the silica gel was first dehydrated in an oven at 200 °C for 4 h until the mass remained constant. The matrix was then cooled down to

ambient temperature before impregnation. Then a volume of an aqueous solution of CaCl_2 at 20 wt%, V_{sol} , corresponding to the volume of the silica gel pores, was added to the matrix. The volume of the solution was determined by Eq. (1) (Courbon et al., 2017).

$$V_{\text{sol}} = V_{p_{\text{matrix}}} \times m_0 \quad (1)$$

With $V_{p_{\text{matrix}}}$ representing the silica gel pore volume and m_0 the mass of anhydrous silica gel.

The silica gel was impregnated for 1 h at ambient temperature. Then the mixture was dried in an oven at 200 °C for 1 h to evaporate the remaining water. The mass of the impregnated material m_1 was obtained. The salt content, SC, can be calculated by Eq. (2) (Courbon et al., 2017; Ye et al., 2013):

$$SC (\%) = \frac{m_1 - m_0}{m_1} \times 100 \quad (2)$$

With m_1 being the mass of the dehydrated composite (silica gel + CaCl_2), and m_0 the mass of anhydrous silica gel.

The impregnation and drying steps were repeated as many times as necessary to reach the desired salt content. This synthesis protocol is described in patent WO/2015/197788 (Courbon et al., 2015) and has already been used for the synthesis of a silica gel/SrBr₂ composite (Courbon et al., 2017).

2.3. X-Ray fluorescence

The salt content was measured by X-ray fluorescence using a Pioneer S4 (Bruker) device. Since the oxygen measurement was not accurate, it was assumed that the oxygen element is only present in SiO_2 and that the overall material was dry. Other elements were considered independently.

2.4. Nitrogen sorption measurements

The specific surface area, the total pore volume, and the average pore diameter of the composite and the pure silica gel were determined through nitrogen sorption measurements at 77 K using a Belsorp max apparatus and the BET determination method. Prior to nitrogen sorption measurements, the sample was dried at 200 °C under a vacuum for 10 h. The total pore volume was determined from the amount adsorbed at $p/p_0 = 0.990$. The specific surface area was estimated using the branch in the relative pressure range from 0.05 to 0.23. The average pore diameter was calculated by assuming that the pores were cylindrical. The pore size distribution was obtained by the Barrett, Joyner and Halenda (BJH) method applied on the nitrogen desorption isotherm.

2.5. SEM – XEDS

The composite was analyzed twice using a Scanning Electron Microscope (SEM) equipped with an X-ray energy-dispersive spectrometry (XEDS) detector, in cross-section and front view. Particles of the composite were encapsulated in a rigid resin that was polished using abrasive paper. Fine polishing was done using a slurry composed of diamond paste and a solvent that did not alter the local composition of the composite. A conductive layer was deposited prior to imaging.

2.6. X-ray diffraction

X-ray thermodiffractometry (XRTD) was performed under air, in a Bruker D8 advance diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.7903 \text{ \AA}$). The temperature range was 30–200 °C, the 2θ angle varied from 8° to 60° with a step of 0.02°. Prior to the measurements, the composite was hydrated under saturated water atmosphere for about 4 h in order to initially form $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ in the composite pores.

2.7. Water sorption isotherms

The water sorption isotherms were measured using dynamic vapor sorption apparatus IGASorp from Hiden Isochema. The measurements were taken between 30 °C and 80 °C. The water vapor was supported by nitrogen. Prior to the measurements, the sample was dried at 200 °C for 10 h under dry nitrogen at atmospheric pressure.

2.8. Efficiency test

The efficiency of the composite for heat storage applications was evaluated on a TG-DSC coupled with a Wetsys humidity generator, from Setaram, with nitrogen as inert gas. Prior to analysis, the sample was dried at 200 °C under a vacuum for 10 h. The sample was first hydrated at 30 °C and 12.5 mbar and was then heated to 80 °C at 12.5 mbar. The mass change (in grams of water per gram of anhydrous composite) between 30 °C and 80 °C at 12.5 mbar is the cycle loading lift of the composite. The desorption temperature was fixed to 80 °C, which is easily attainable by solar thermal collectors. The sorption temperature was fixed to 30 °C, which is sufficient for space heating applications. The water vapor pressure was fixed to 12.5 mbar, which corresponds first to saturation vapor pressure at 10 °C, chosen as reference value for evaporation and condensation pressures in a closed system, and second to 50% of relative humidity (RH) at 20 °C, representative of an open system. The heat of sorption was obtained by integration of the heat flow signal. Corrections had to be done as the experiment was carried out under a temperature change. The corrections took into account the heat required to heat the crucibles and the composite. The heat of sorption is calculated by Eq. (3):

$$\Delta H_{\text{sorption}} (\text{J/g}) = \frac{\Delta H_{\text{exp}} (\text{mJ}) - \Delta H_{\text{crucible}} (\text{mJ}) - mc_p \Delta T (\text{mJ})}{m (\text{mg})} \quad (3)$$

With ΔH_{exp} being the integration of the heat flow signal during the test on the composite, $\Delta H_{\text{crucible}}$ the integration of the heat flow signal during a blank test (empty crucibles), m the mass of anhydrous composite, c_p the heat capacity of the composite, and ΔT the rise in temperature during the test (50 °C).

Considering the heat of sorption and the experimental packing density of the anhydrous composite, the energy storage density (in kW h/m^3) can be calculated.

2.9. Multi-cycles stability

The stability of the composite after 10 successive sorption/desorption cycles was evaluated on the dynamic vapor sorption apparatus, IGASorp from Hiden Isochema. The sample was first dried at 200 °C under dry nitrogen for 10 h. The sample was then submitted to successive adsorptions at 30 °C and 29.5% RH and at 80 °C and 2.6% RH (both values of humidity corresponding to water vapor pressure of 12.5 mbar). The sample was dried under dry nitrogen after each adsorption step.

3. Results and discussion

The synthesis protocol used in this study differs from those previously reported in the literature. For those composites, the preparation implied impregnation with a large quantity of salt solution followed by a filtration step to remove the excess salt, sometimes followed by a washing step with water or ethanol, before drying in an oven (Aristov et al., 2002, 1997, 1996a, 1996b; Gordeeva et al., 2006; Tokarev and Aristov, 1997; Wu et al., 2007; Zheng et al., 2014). The present protocol used in this study used successive impregnations of a small quantity of salt solution (corresponding to the matrix pore volume) and drying steps, thereby leading to composites with a high salt content. The silica gel/ CaCl_2 composite synthesized with this new protocol (i.e. SG62/

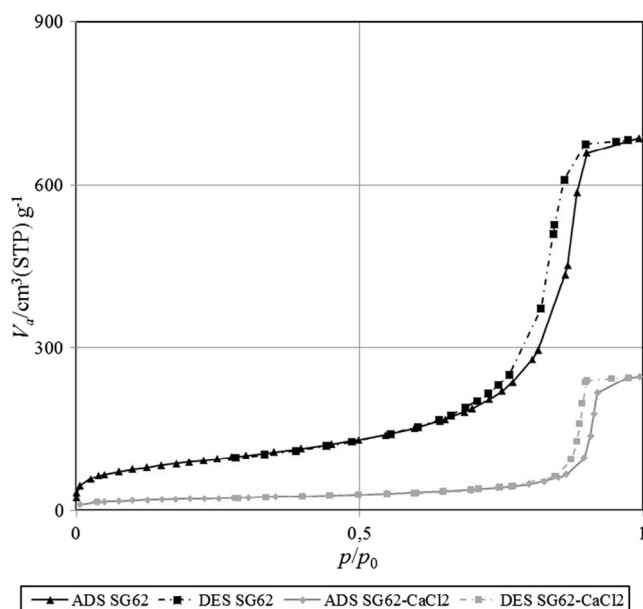


Fig. 1. Nitrogen adsorption (continuous line) and desorption (dotted line) isotherms at 77 K of silica gel SG62 (black) and SG62/CaCl₂ 43 wt% composite (grey).

CaCl₂) presented a CaCl₂ content of 43 wt% obtained by mass difference during the synthesis. This salt content was confirmed by X-ray fluorescence, which gave a salt content of 44 ± 2 wt%. This high salt content was achieved previously in composites based on mesoporous silica like SBA-15 (Ponomarenko et al., 2010) or MCM-41 (Ponomarenko et al., 2010), but the synthesis of these silica gels is too expensive to be scaled up for storage systems. In contrast to SBA-15 or MCM-41, the silica gel used in the present study is commercially available in large quantities and is thus particularly appropriate for seasonal energy storage applications.

Concerning nitrogen sorption measurement (Fig. 1), both pure silica gel and the SG62/CaCl₂ 43 wt% composite exhibit adsorption isotherms typical of mesoporous materials with capillary condensation occurring at high relative pressure. The hysteresis between the adsorption and desorption isotherms occurs in a narrow pressure range. The closure point of the hysteresis occurs at higher relative pressure for SG62/CaCl₂ 43 wt% compared to pure silica gel, indicating an increase of the pore size in agreement with the pore size distribution obtained by the BJH method (Fig. 2). According to the pore size distribution, it seems that the smallest pores of the matrix were completely filled by the salt, while the largest ones were only partially filled by the salt. This residual porosity favors a free access for water vapor. A similar location of the salt in the silica gel pores had already been observed in composite SG62/SrBr₂ synthesized with the same protocol (Courbon et al., 2017). As for the SG62/SrBr₂ composite (Courbon et al., 2017), the presence of larger pores in the composite compared to the pure matrix is surprising. A difference of interaction between N₂ molecules and the surface of the composite containing salt, or the hypothesis of cylindrical pores, could explain this phenomenon.

The comparison of the structural characteristics (specific surface area, total pore volume and average pore diameter) of the composite and silica gel (Table 1) shows a decrease of the surface area and total pore volume with the incorporation of the salt into the matrix. This confirms the presence of the salt inside the pores of the matrix and not only on the surface of the silica particles.

Considering the pore volumes of the matrix and composite, the salt content, SC_{BET} , can be calculated, assuming that the salt occupies the difference of volume between the matrix and composite pore volumes. This salt content is calculated using the following equation, where V_p is the pore volume and ρ_{salt} the density of anhydrous CaCl₂ ($2.15 \text{ cm}^3/\text{g}$):

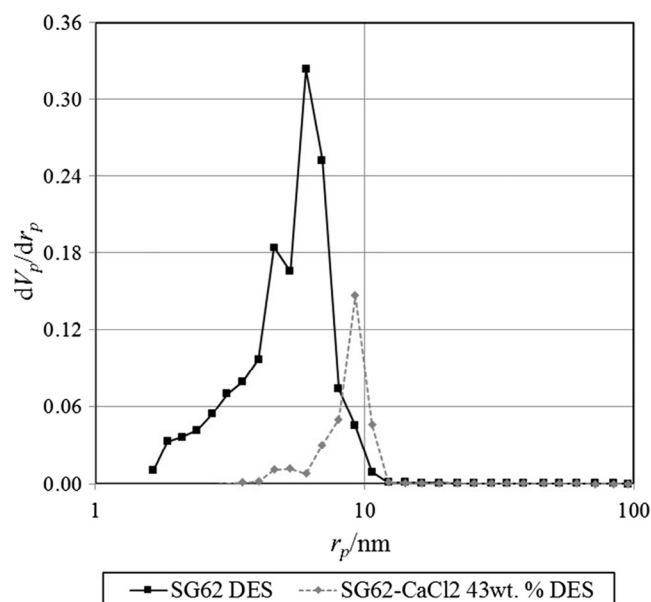


Fig. 2. Pore size distribution obtained by BJH analysis from the nitrogen desorption isotherm at 77 K for pure silica gel SG62 (black line) and SG62/CaCl₂ 43 wt% composite (grey dotted line).

Table 1

Structural characteristics of silica gel SG62 and composite SG62/CaCl₂ 43 wt% obtained from BET analysis of nitrogen adsorption isotherm at 77 K.

	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
SG62	320	1.06	13
SG62/CaCl ₂ 43 wt%	75	0.38	20

$$SC_{BET} = \frac{V_{P_{matrix}} - V_{P_{composite}}}{V_{P_{matrix}} + \frac{1}{\rho_{salt}}} \quad (4)$$

According to this equation, the salt content of the composite SG62/CaCl₂ is 44 wt%, which is fully consistent with that of the experimental salt content obtained by mass difference and that measured by X-ray fluorescence. This indicates that the difference of pore volume between the composite and the matrix is only due to the presence of salt.

SEM observations coupled with elemental analysis confirm the location of salt in the pores of the silica gel, with a good homogeneity inside the particles. A front view shows the unaltered morphology of the silica particles with the expected size, and no additional crystallites of salt. The particles are deeply impregnated, and the concentrations of Ca and Cl at the center of the particle are sometimes even higher than on the borders (Fig. 3). This is shown by elemental mapping (Fig. 3(c and d)).

The water vapor sorption isotherms of the composite were evaluated between 30 °C and 80 °C (Fig. 4). Considering a given isotherm, a first water uptake was observed, followed by a plateau at around 0.14 g/g. A second water uptake was then observed, followed by a linear increase of the mass with pressure. A hysteresis between adsorption and desorption was observed for every temperature. In order to understand the behavior of the salt in this mechanism of sorption, X-ray diffraction patterns were recorded by varying the temperature on the SG62/CaCl₂ composite (Fig. 5). Before recording the XRD diagram, the SG62/CaCl₂ composite was exposed for about 4 h to a saturated water atmosphere in order to prepare a composite with a high hydration rate (i.e. CaCl₂·4H₂O). Between 30 °C and 50 °C, no X-ray diffraction peaks were observed showing that the CaCl₂ is amorphous or liquid, while crystalline CaCl₂·4H₂O was expected. This indicates the

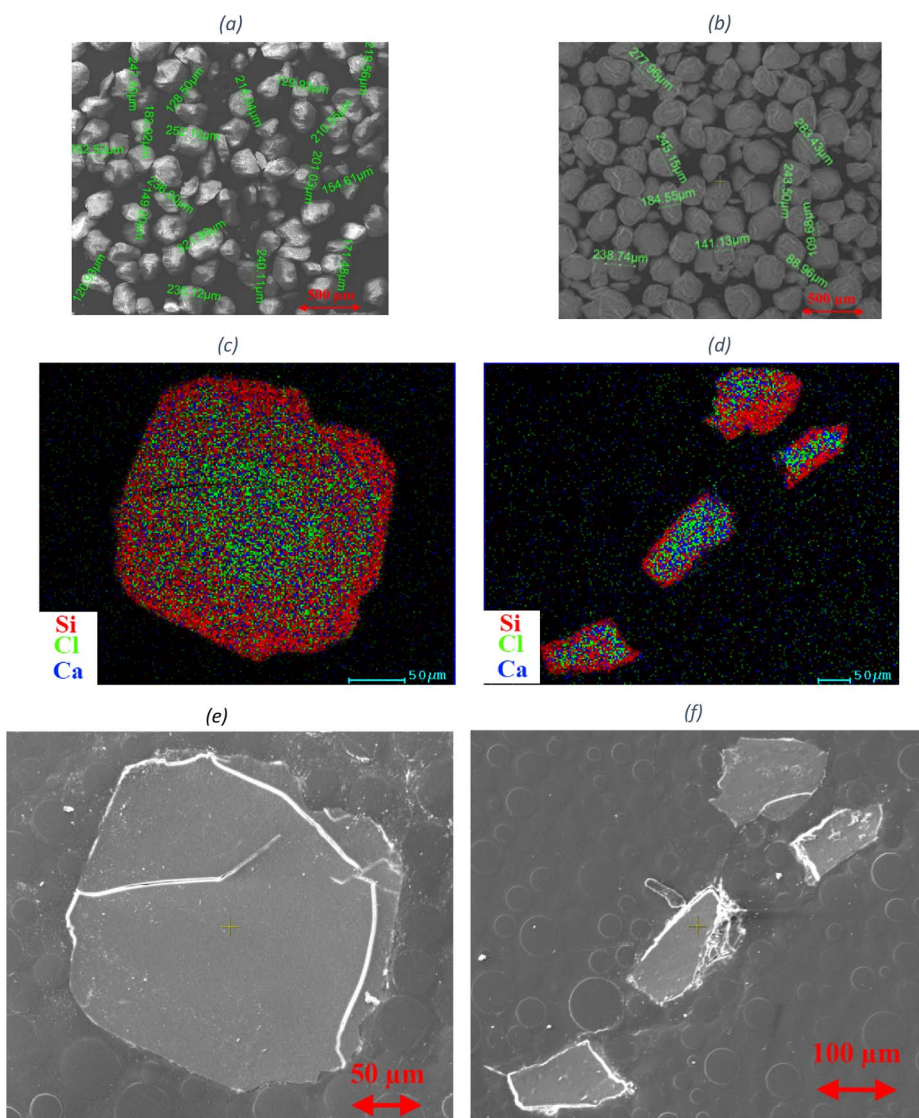


Fig. 3. SEM Images of (a) Composite SG62/CaCl₂ particles; (b) silica gel particles; (c) and (d) elemental mapping of silicon (red), calcium (blue) and chlorine (green) by XEDS for the SG62/CaCl₂ particles indicated by SEM cross-section images (e) and (f).

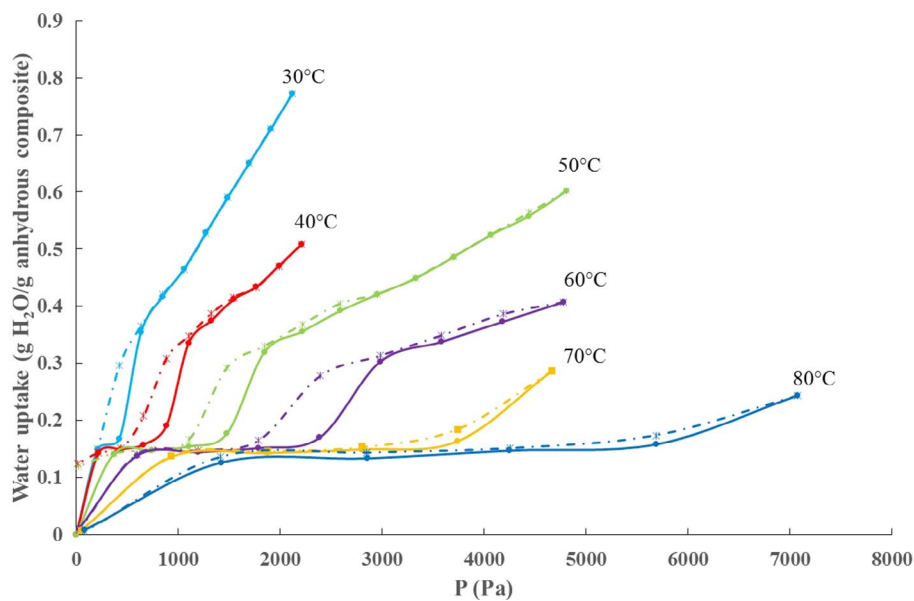


Fig. 4. Water vapor sorption isotherms of composite SG62/CaCl₂ 43 wt%. Adsorption isotherms are represented by continuous lines whereas desorption isotherms are represented by discontinuous lines.

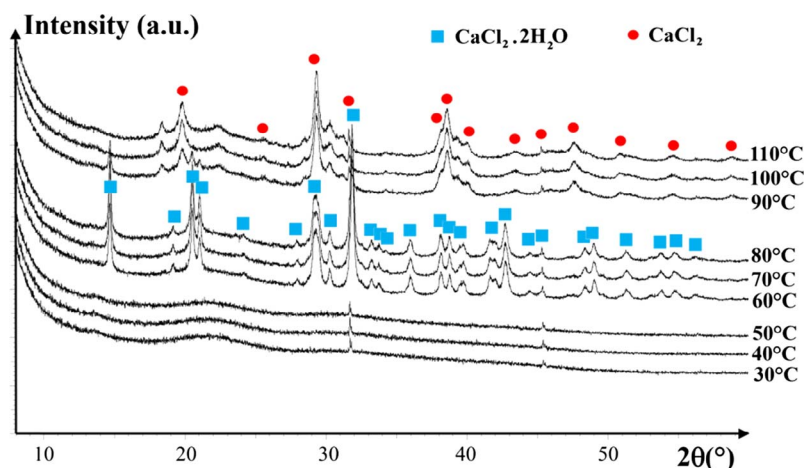
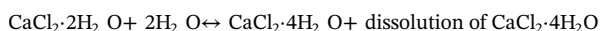
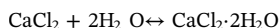


Fig. 5. Temperature dependent X-ray diffraction patterns of SG62/CaCl₂ 43 wt%. Above 110 °C, no more change in the diffraction patterns is observed. At ≥ 90 °C, small peaks at $2\theta = 18.3^\circ$, 22.3° , 30.2° and 39.3° cannot be indexed with certainty.

dissolution of CaCl₂·4H₂O in the composite. Between 60 °C and 80 °C, the dihydrate form of CaCl₂ was observed, and, for temperatures higher than 90 °C, anhydrous CaCl₂ was mainly observed. The monohydrate form of CaCl₂ was not observed whatever the temperature. This explains the water vapor sorption behavior of this composite: first, the hydration reaction of CaCl₂ into CaCl₂ dihydrate occurs followed by the hydration reaction to the CaCl₂ tetrahydrate, which dissolves to form a CaCl₂ solution. Then the absorption of water in the CaCl₂ solution trapped in the pores of silica gel occurs. The hysteresis observed between the sorption and desorption steps is hence explained by the recrystallization step.



Absorption of water by the CaCl₂ solution trapped in the silica gel pores

This mechanism is also confirmed by the comparison between the water sorption isotherms of SG62/CaCl₂ 43 wt% and of pure CaCl₂ at 30 °C (expressed in number of moles of water adsorbed per mole of CaCl₂) (Fig. 6). The first plateau of the composite isotherm corresponds to the adsorption of 2 mol of water per mole of CaCl₂ of the composite. Moreover, the last part of the composite isotherm corresponds exactly to the absorption of water in the CaCl₂ solution (OxyCalciumChloride, n.d.). Consistently with XRD patterns, this confirms that salt solution is formed in the pores of silica gel from the tetrahydrate CaCl₂, and then the water sorption mechanism is the absorption in the salt solution.

The silica gel was not involved in the water vapor sorption of the

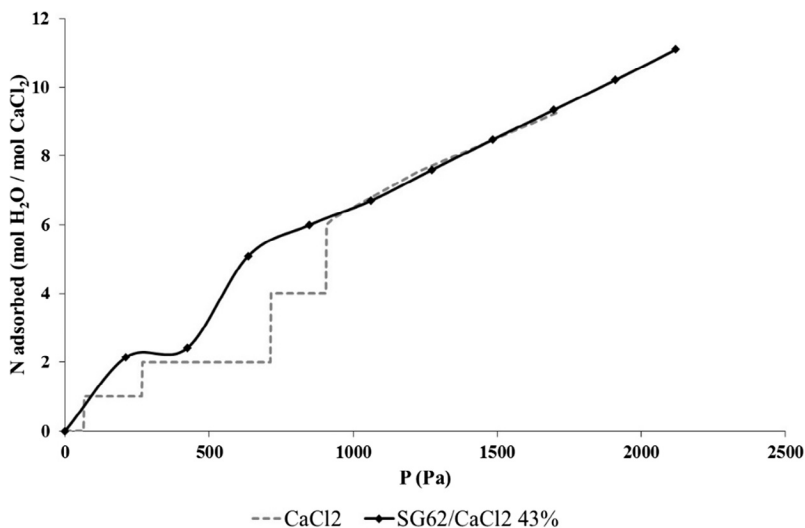


Fig. 6. Comparison of sorption isotherms at 30 °C of pure CaCl₂ (grey dotted line) and composite SG62/CaCl₂ 43 wt% (black line) expressed in mol H₂O/mol CaCl₂.

composite. This confirms that the salt content directly impacts the sorption performance of the composite. Therefore, the higher the salt content, the better the sorption performance. However, the thermodynamic equilibrium data of pure salt is modified when salt is incorporated into the matrix.

As far as sorption capacity is concerned, composite SG62/CaCl₂ 43 wt% has interesting sorption properties. It can adsorb 0.77 g/g at 30 °C and 50% RH (21 mbar). When comparing the sorption isotherms of SG62/CaCl₂ 43 wt% to those of other composites previously reported at 50 °C (Fig. 7), an increase of the water uptake is observed in comparison to SWS1L or composites based on SBA15 at around 29 wt%, which were obtained through SBA with different pore sizes (8.1 nm and 11.8 nm) (Glaznev et al., 2011), as a result of the high salt content of SG62/CaCl₂ 43 wt%. Compared to MCM-41/CaCl₂ at 42 wt%, SG62/CaCl₂ 43 wt% adsorbs more water at high water vapor pressure (> 1800 Pa). The sorption properties of the composite SG62/CaCl₂ 43 wt% used here and SBA15/CaCl₂ 43 wt% are very close at 50 °C; however, no information is given concerning the behavior of SBA15/CaCl₂ 43 wt% at other temperatures and its stability over successive sorption/desorption cycles.

As far as solar heat storage coupled with space heating is concerned, the difference of mass between adsorption conditions (representative of the winter heat release mode) and desorption conditions (representative of the summer heat storage mode) is the most relevant parameter for evaluating the performance of thermochemical storage materials. In this work, this mass difference corresponds to the cycle loading lift. Here the adsorption temperature was chosen as 30 °C and

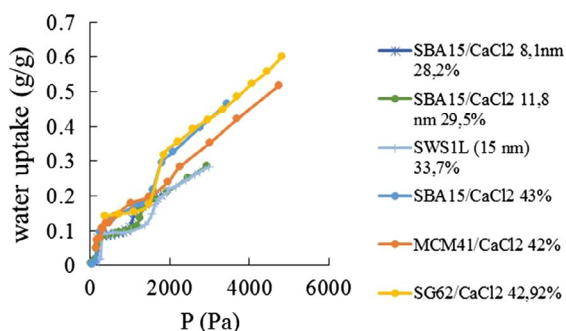


Fig. 7. Comparison of water vapor sorption isotherms at 50 °C of SBA15 (8.1 nm)/CaCl₂ 28.2 wt% (Glaznev et al., 2011), SBA15 (11.8 nm)/CaCl₂ 29.5 wt% (Glaznev et al., 2011), SWS1L/CaCl₂ 33.7 wt% (Glaznev et al., 2011), SBA15/CaCl₂ 43 wt% (Ponomarenko et al., 2010), MCM41/CaCl₂ 42 wt% (Ponomarenko et al., 2010) and SG62/CaCl₂ 43 wt %.

the desorption temperature 80 °C; the vapor pressure was taken to be 12.5 mbar.

In these conditions, the experimental cycle loading lift is 0.40 g/g, which corresponds to an energy storage capacity of 300 W h/kg, and an energy storage density of 211 kW h/m³ for the bed of anhydrous composite. The energy storage density is calculated according to the experimental packing density of the anhydrous composite, which is 703 kg/m³. This energy storage density is significantly higher than that of composites previously reported for the same application but with higher desorption temperature. For the zeolite 13X/MgSO₄ composite, the energy storage density is only 166 kW h/m³ between 30 °C and 150 °C at 17–19 mbar (Hongois et al., 2011). For composites based on aluminosilicate and CaCl₂, only 180 kW h/m³ was reached between 20 °C and 150 °C at 7.8 mbar (Jabbari-Hichri et al., 2015). This high energy storage density makes this SG62/CaCl₂ composite at 43 wt% a promising candidate for solar heat storage coupled with space heating. It is noteworthy that any increase of the desorption temperature would increase the energy storage density.

In order to evaluate the performance of this composite in storage systems, it is important to be able to predict the water uptake for different temperature and pressure conditions. Indeed, for the evaluation of the performance of composite, reference conditions were chosen that are representative of storage systems working conditions. However, in real systems, temperature and pressure may vary to some extent, thereby influencing the water sorption properties of composites. A mathematical model was therefore proposed here, which aims to accurately describe the experimental data to be used in storage system models, and not to explain the sorption mechanism. To determine this mathematical model, the characteristic curve (adsorbed volume vs. adsorption potential) based on the Polanyi theory (Polanyi, 1932, 1929) was plotted (Fig. 8). To simplify the calculations, the water density was fixed to 1 g/cm³, the adsorbed volume therefore equals the adsorbed mass.

A mathematical model was determined thanks to Table Curve 2D v4 software, excluding the experimental points for adsorption potential higher than 16000 J/mol:

$$y = \frac{a + cx^{0.5} + ex + gx^{1.5}}{1 + bx^{0.5} + dx + fx^{1.5} + hx^2} \quad (5)$$

where y is the adsorbed volume (or the adsorbed mass), and x is the adsorption potential:

$$x = RT \times \ln\left(\frac{p_0}{p}\right) \quad (6)$$

The parameters of this mathematical model are presented in Table 2. Fitting performances are given in Fig. 9.

Thanks to this model, the water uptake at different temperature and pressure conditions could be calculated and as such, the influence of

these parameters on the cycle loading lift and energy storage density could be evaluated. Fig. 10 presents the cycle loading lift and the energy storage density for different adsorption temperatures (ranging from 20 °C to 40 °C), for a desorption temperature of 80 °C and a water vapor pressure of 12.5 mbar. As expected, the lower the adsorption temperature, the higher the composite sorption performance. Between 30 °C and 80 °C at 12.5 mbar, the calculated cycle loading lift is 0.39 g/g, which agrees with the experimental results. The cycle loading lift decreases to 0.24 g/g at an adsorption temperature equal to 40 °C, leading to an energy storage density of 126 kW h/m³. Extrapolating the calculation to an adsorption temperature of 20 °C, the cycle loading lift is high with a value of 0.72 g/g, which corresponds to an energy storage density of 382 kW h/m³. The adsorption temperature has a considerable influence on the performance of the composite SG62/CaCl₂ 43 wt %.

The water vapor pressure also influences the cycle loading lift, and hence the energy storage density, as can be observed in Fig. 11. As expected, the higher the desorption pressure, the lower the composite performance. With a desorption pressure of 12.5 mbar, the cycle loading lift is 0.39 g/g and the energy storage density is 207 kW h/m³, whereas with a desorption pressure of 30 mbar, the cycle loading lift decreases to 0.365 g/g, which corresponds to an energy storage density of 193 kW h/m³.

The temperature and pressure conditions of the storage system will influence the composite performance. Nevertheless, in the reference conditions, the composite exhibits a high cycle loading lift and promising energy storage density. It is interesting to note that any increase of the desorption temperature and/or any decrease of the adsorption temperature will increase the performance of the composite (its energy storage density) and thus promote its applicability for seasonal heat storage coupled to space heating applications.

The cycle loading lift in the adsorption and desorption steps for 10 successive cycles are presented in Fig. 12. The sorption performance of the composite shows an excellent stability with the absence of any performance loss over 10 successive sorption/desorption cycles. This confirms that this composite is a very promising candidate for thermal heat storage for space heating applications. The enhanced stability under cycles shows that the high salt content does not affect the stability in the cycles and thus the performance of the composite for heat storage applications. No leaching of the salt solution from the matrix is evidenced under the operating conditions of a heat storage system. This is particularly remarkable as at 30 °C and 12.5 mbar, the salt is solubilized in the pores of silica gel. This demonstrates that the silica matrix is able to create a stabilizing microenvironment for calcium chloride through specific interactions and a confinement effect. Moreover, it confirms the efficiency of the synthesis protocol to produce a composite with a high salt content, high energy storage density, and high stability.

4. Conclusion

An original synthesis protocol to produce a silica gel composite with high salt content CaCl₂ was developed using successive impregnation of small amounts of salt solution (corresponding to the pore volume of silica gel) and drying steps. This novel synthesis protocol leads to composites that combine both a high salt content (i.e. 43 wt% CaCl₂) and high stability, which are both requirements for the practical use of composites for seasonal storage applications. Moreover, this composite has a very promising performance in the conditions of a thermochemical storage system coupled with space heating (between 30 °C and 80 °C at 12.5 mbar). The cycle loading lift is 0.40 g/g, which corresponds to an energy storage capacity of 300 W h/kg and an energy storage density of 211 kW h/m³ (considering the packing density). These results outperform those previously reported for composites based on aluminosilicate and CaCl₂ (180 kW h/m³ between 20 °C and 150 °C at 7.8 mbar), as well as composites based on zeolite 13X and MgSO₄ (166 kW h/m³ between 30 °C and 150 °C at 17–19 mbar). In

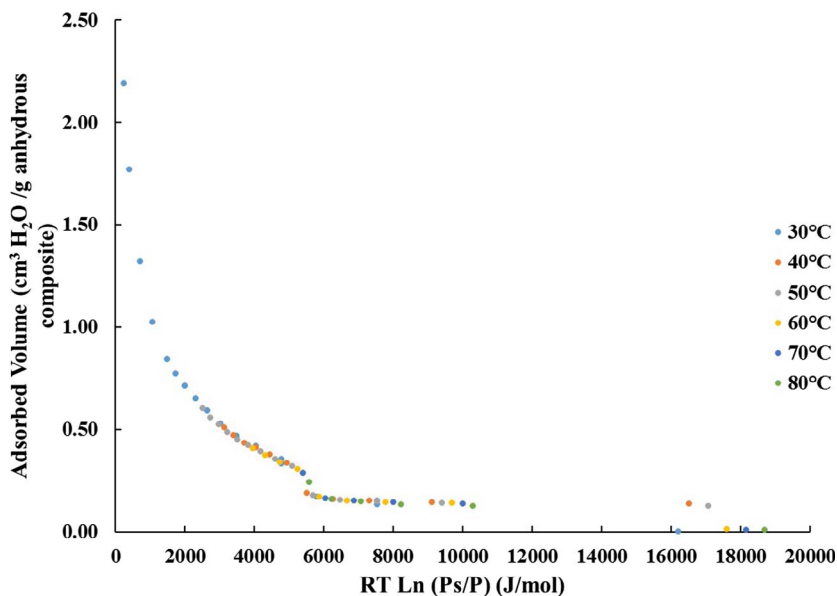


Fig. 8. Characteristic curve derived from adsorption isotherms of composite SG62/CaCl₂ 43 wt%.

Table 2
Parameters of the mathematical model.

Parameter	Value
a	7.245114913
b	0.081869322
c	-0.21981027
d	-0.00131786
e	0.002066184
f	-0.000016095
g	-5.5829E-06
h	2.27088E-07
R ²	0.9988

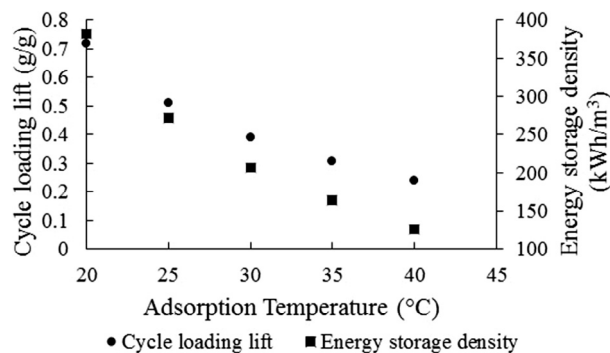


Fig. 10. Influence of adsorption temperature on the cycle loading lift and energy storage density with desorption temperature = 80 °C and water vapor pressure = 12.5 mbar.

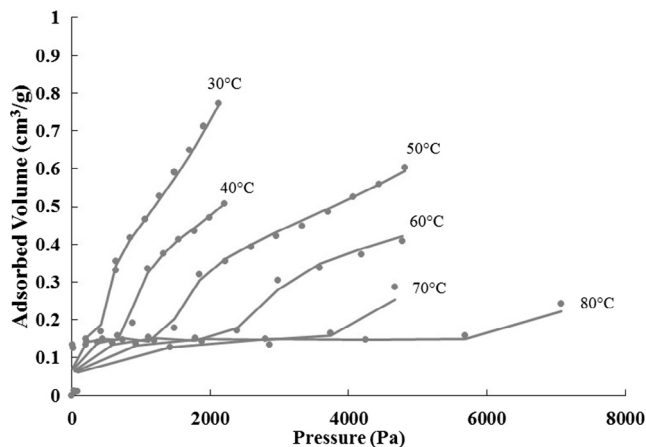


Fig. 9. Comparison between the experimental data (points) and simulated data (line) of adsorption isotherms of SG62/CaCl₂ 43 wt%.

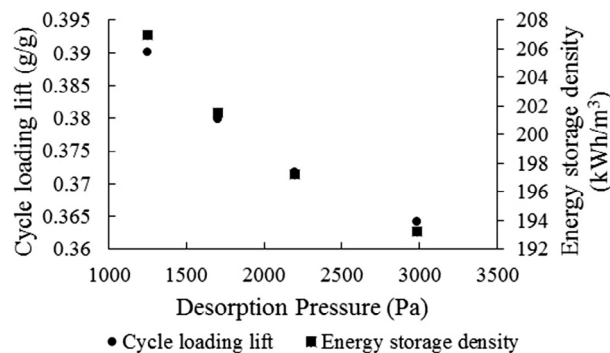


Fig. 11. Influence of the desorption pressure (condensation pressure in a closed system) on the cycle loading lift and energy storage density with adsorption at 30 °C and 1250 Pa and desorption at 80 °C.

contrast to numerous composites reported in the literature, it is remarkable that the silica gel/CaCl₂ composite of the present study presents such interesting properties, even at a particularly low desorption temperature, which is more appropriate for the use of solar thermal collectors. Moreover, the cycle loading lift of SG62/CaCl₂ 43 wt% is constant after 10 cycles, showing excellent stability of the composites upon cycles. Such results may be explained as followed:

- (i) The salt content is high, due to the impregnation protocol and thanks to the high pore volume of the matrix.

- (ii) The mechanism of water sorption does not only involve the hydration from CaCl₂ to CaCl₂·2H₂O and to CaCl₂·4H₂O, but also the exothermic dissolution of CaCl₂, and subsequent absorption of water by the solution into the pores.
- (iii) The salt is homogeneously distributed in the silica gel pores with the absence of its recrystallization on the surface of the silica particles.

Based on the measurements of water sorption isotherms between 30 °C and 80 °C, a mathematical model was proposed to describe the

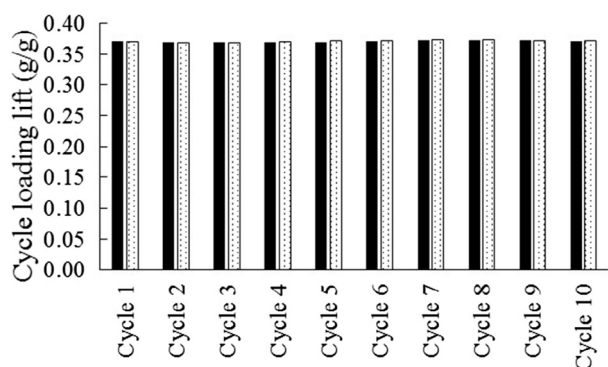


Fig. 12. Stability of the cycle loading lift of composite SG62/CaCl₂ 43 wt% after 10 successive sorption/desorption cycles; desorption step: between 30 °C and 80 °C at 12.5 mbar, in black; adsorption step: between 80 °C and 30 °C at 12.5 mbar, in black points.

water sorption data in the tested conditions. In particular, the cycle loading lift increases by decreasing the desorption pressure or the adsorption temperature.

The complete characterization of this composite material enables us to predict and control its behavior in heat storage reactor. This composite was tested in laboratory prototypes, whose results will be published soon in two future publications. It was also used in two real-scale systems, developed in the FP7 SoTherCo project, tested in Arlon (Belgium) and Le Bourget du Lac (France). All these tests confirm the possibility to use this composite in heat storage systems for space heating applications.

Acknowledgements

The authors gratefully acknowledge the financial support of the European Commission within the FP7 program under grant No. 295775 (Project ENER/FP7EN/295775/“Sotherco”). The authors would also like to thank Solvay for providing Caso® granules. Thanks also go to Christian Serre, for the access to the XRD equipment at Institut Lavoisier, University of Versailles Saint-Quentin-en-Yvelines. The authors would also like to thank Natalie Dickson for her corrections and suggestions.

References

Aristov, Y.I., Marco, G., Tokarev, M.M., Parmon, V.N., 1997. Selective water sorbents for multiple applications, 3. CaCl₂ solution confined in micro- and mesoporous silica gels: pore size effect on the “solidification-melting” diagram. *React. Kinet. Catal. Lett.* 61, 147–154. <http://dx.doi.org/10.1007/BF02477527>.

Aristov, Y.I., Restuccia, G., Cacciola, G., Parmon, V.N., 2002. A family of new working materials for solid sorption air conditioning systems. *Appl. Therm. Eng.* 22, 191–204. [http://dx.doi.org/10.1016/S1359-4311\(01\)00072-2](http://dx.doi.org/10.1016/S1359-4311(01)00072-2).

Aristov, Y.I., Tokarev, M.M., Restuccia, G., Cacciola, G., 1996a. Selective water sorbents for multiple applications, 2. CaCl₂ confined in micropores of silica gel: sorption properties. *React. Kinet. Catal. Lett.* 59, 335–342. <http://dx.doi.org/10.1007/Bf02068131>.

Aristov, Y.I., Tokarev, M.M., Restuccia, G., Cacciola, G., Aristov, Yu.I.G., Restuccia, G., Cacciola, M.T., 1996b. Selective water sorbents for multiple applications, 1. CaCl₂ confined in mesopores of silica gel: sorption properties. *React. Kinet. Catal. Lett.* 59, 325–333. <http://dx.doi.org/10.1007/BF02475434>.

Aydin, D., Casey, S.P., Riffat, S., 2015. The latest advancements on thermochemical heat storage systems. *Renew. Sustain. Energy Rev.* 41, 356–367. <http://dx.doi.org/10.1016/j.rser.2014.08.054>.

Bouché, M., Richter, M., Linder, M., 2016. Heat transformation based on CaCl₂/H₂O – Part B: Open operation principle. *Appl. Therm. Eng.* 102, 641–647. <http://dx.doi.org/10.1016/j.applthermaleng.2016.03.102>.

Courbon, E., D’Ans, P., Permyakova, A., Skrylnyk, O., Steunou, N., Degrez, M., Frère, M., 2017. A new composite sorbent based on SrBr₂ and silica gel for solar energy storage application with high energy storage density and stability. *Appl. Energy* 190, 1184–1194.

Courbon, E., Frère, M., Heymans, N., D’Ans, P., 2015. Hygroscopic composite material. WO2015197788.

De Jong, A.J., Trausel, F., Finck, C., Van Vliet, L., Cuypers, R., 2014. Thermochemical heat storage – system design issues. *Energy Procedia* 309–319. <http://dx.doi.org/10.1016/j.egypro.2014.02.036>.

Donkers, P.A.J., Pel, L., Adan, O.C.G., 2016. Experimental studies for the cyclability of salt hydrates for thermochemical heat storage. *J. Energy Storage* 5, 25–32. <http://dx.doi.org/10.1016/j.est.2015.11.005>.

Elsayed, A., Elsayed, E., AL-Dadah, R., Mahmoud, S., Elshaer, A., Kaialy, W., 2016. Thermal energy storage using metal–organic framework materials. *Appl. Energy*. <http://dx.doi.org/10.1016/j.apenergy.2016.03.113>.

Ferchaud, C.J., Scherpenborg, R.A.A., Zondag, H.A., De Boer, R., 2014. Thermochemical seasonal solar heat storage in salt hydrates for residential applications – influence of the water vapor pressure on the desorption kinetics of MgSO₄·7H₂O. *Energy Procedia* 2436–2440. <http://dx.doi.org/10.1016/j.egypro.2014.10.252>.

Ferchaud, C.J., Zondag, H.A., De Boer, R., 2013. Material research on salt hydrates for seasonal heat storage application in a residential environment. In: *Proceedings of International Symposium on Innovative Materials for Processes in Energy Systems – IMPRES2013*, pp. 73.

Ferchaud, C.J., Zondag, H., De Boer, R., Rindt, C.C.M., 2012. Characterization of the sorption process in thermochemical materials for seasonal heat storage application. In: *Proceedings of Innostock, Lleida*.

Fopah Lele, A., Kuznik, F., Opel, O., Ruck, W.K.L., 2015. Performance analysis of a thermochemical based heat storage as an addition to cogeneration systems. *Energy Convers. Manage.* 106, 1327–1344. <http://dx.doi.org/10.1016/j.enconman.2015.10.068>.

Glaznev, I., Ponomarenko, I., Kirik, S., Aristov, Y., 2011. Composites CaCl₂/SBA-15 for adsorptive transformation of low temperature heat: pore size effect. *Int. J. Refrig.* 1244–1250. <http://dx.doi.org/10.1016/j.ijrefrig.2011.02.007>.

Gordeeva, L.G., Glaznev, I.S., Savchenko, E.V., Malakhov, V.V., Aristov, Y.I., 2006. Impact of phase composition on water adsorption on inorganic hybrids “salt/silica”. *J. Colloid Interface Sci.* 301, 685–691. <http://dx.doi.org/10.1016/j.jcis.2006.05.009>.

Gordeeva, L.G., Mrowiec-Bialon, J., Jarzebski, A.B., Lachowski, A.I., Malinowski, J.J., Aristov, Y.I., 1999. Selective water sorbents for multiple applications, 8. sorption properties of CaCl₂–SiO₂ sol-gel composites. *React. Kinet. Catal. Lett.* 66, 113–120. <http://dx.doi.org/10.1007/BF02475749>.

Hennaut, S., Thomas, S., Davin, E., Skrylnyk, A., Frère, M., André, P., 2014. Simulation of a vertical ground heat exchanger as low temperature heat source for a closed adsorption seasonal storage of solar heat. *Energy Procedia* 370–379.

Hongois, S., Kuznik, F., Stevens, P., Roux, J.-J., 2011. Development and characterisation of a new MgSO₄–zeolite composite for long-term thermal energy storage. *Sol. Energy Mater. Sol. Cells* 95, 1831–1837.

Jabbari-Hichri, A., Bennici, S., Auroux, A., 2015. Enhancing the heat storage density of silica–alumina by addition of hygroscopic salts (CaCl₂, Ba(OH)₂, and LiNO₃). *Sol. Energy Mater. Sol. Cells* 140, 351–360. <http://dx.doi.org/10.1016/j.solmat.2015.04.032>.

Ji, J.G., Wang, R.Z., Li, L.X., 2007. New composite adsorbent for solar-driven fresh water production from the atmosphere. *Desalination* 212, 176–182. <http://dx.doi.org/10.1016/j.desal.2006.10.008>.

Lahmidi, H., Mauran, S., Goetz, V., 2006. Definition, test and simulation of a thermochemical storage process adapted to solar thermal systems. *Sol. Energy* 80, 883–893. <http://dx.doi.org/10.1016/j.solener.2005.01.014>.

Michel, B., Mazet, N., Mauran, S., Stitou, D., Xu, J., 2012. Thermochemical process for seasonal storage of solar energy: characterization and modeling of a high density reactive bed. *Energy* 47, 553–563. <http://dx.doi.org/10.1016/j.energy.2012.09.029>.

Michel, B., Mazet, N., Neveu, P., 2014. Experimental investigation of an innovative thermochemical process operating with a hydrate salt and moist air for thermal storage of solar energy: global performance. *Appl. Energy* 129, 177–186. <http://dx.doi.org/10.1016/j.apenergy.2014.04.073>.

Mugnier, D., Goetz, V., 2001. Energy storage comparison of sorption systems for cooling and refrigeration. *Sol. Energy* 71, 47–56. [http://dx.doi.org/10.1016/S0038-092X\(01\)00013-5](http://dx.doi.org/10.1016/S0038-092X(01)00013-5).

N’Tsoukpoe, K.E., Liu, H., Le Pierrès, N., Luo, L., 2009. A review on long-term sorption solar energy storage. *Renew. Sustain. Energy Rev.* <http://dx.doi.org/10.1016/j.rser.2009.05.008>.

N’Tsoukpoe, K.E., Schmidt, T., Rammelberg, H.U., Watts, B.A., Ruck, W.K.L., 2014. A systematic multi-step screening of numerous salt hydrates for low temperature thermochemical energy storage. *Appl. Energy* 124, 1–16. <http://dx.doi.org/10.1016/j.apenergy.2014.02.053>.

OxyCalciumChloride, n.d. Calcium chloride: a guide to physical properties.

Permyakova, A., Skrylnyk, O., Courbon, E., Affram, M., Wang, S., Lee, U.-H., Valekar, A.H., Nouar, F., Mouchaham, G., Devic, T., De Weireld, G., Chang, J.-S., Steunou, N., Frère, M., Serre, C., 2017. Synthesis optimization, shaping and heat reallocation evaluation of the hydrophilic Metal Organic Framework MIL-160(Al). *Chemosuschem.* <http://dx.doi.org/10.1002/cssc.201700164>.

Polanyi, M., 1932. *Trans. Faraday Soc.* 28, 316.

Polanyi, M., 1929. *Elektrochem* 35, 431.

Ponomarenko, I.V., Glaznev, I.S., Gubar, A.V., Aristov, Y.I., Kirik, S.D., 2010. Synthesis and water sorption properties of a new composite “CaCl₂ confined into SBA-15 pores”. *Microporous Mesoporous Mater.* 129, 243–250. <http://dx.doi.org/10.1016/j.micromeso.2009.09.023>.

Ristić, A., Maučec, D., Henninger, S.K., Kaučič, V., 2012. New two-component water sorbent CaCl₂-FeKIL₂ for solar thermal energy storage. *Microporous Mesoporous Mater.* 164, 266–272. <http://dx.doi.org/10.1016/j.micromeso.2012.06.054>.

Solé, A., Fontanet, X., Barreneche, C., Martorell, I., Fernández, A.I., Cabeza, L.F., 2012. Parameters to take into account when developing a new thermochemical energy storage system. *Energy Procedia* 380–387. <http://dx.doi.org/10.1016/j.egypro.2012.11.045>.

Tohidi, S.H., Ziaie, F., Abdolmaleki, A., 2009. Preparation and characterization of SiO₂-CaCl₂ nanocomposite by the sol-gel method. *Int. J. Eng. Trans. B: Appl.* 22.

- Tokarev, M., Gordeeva, L., Romannikov, V., Glaznev, I., Aristov, Y., 2002. New composite sorbent CaCl_2 in mesopores for sorption cooling/heating. *Int. J. Therm. Sci.* 41, 470–474. [http://dx.doi.org/10.1016/S1290-0729\(02\)01339-X](http://dx.doi.org/10.1016/S1290-0729(02)01339-X).
- Tokarev, M.M.M., Aristov, Y.I., 1997. Selective water sorbents for multiple applications, 4. CaCl_2 confined in silica gel pores: sorption/desorption kinetics. *React. Kinet. Catal. Lett.* 62, 143–150. <http://dx.doi.org/10.1007/BF02475725>.
- Trausel, F., De Jong, A.J., Cuypers, R., 2014. A review on the properties of salt hydrates for thermochemical storage. *Energy Procedia* 447–452. <http://dx.doi.org/10.1016/j.egypro.2014.02.053>.
- van Essen, V.M., Cot Gores, J., Bleijendaal, L.P.J., Zondag, H.A., Schuitema, R., Bakker, M., van Helden, W.G.J., 2009a. Characterization of salt hydrates for compact seasonal thermochemical storage. In: *ASME 2009 3rd Int. Conf. Energy Sustain.*, vol. 2 2. pp. 825–830.
- van Essen, V.M., Zondag, H.a., Gores, J.C., Bleijendaal, L.P.J., Bakker, M., Schuitema, R., van Helden, W.G.J., He, Z., Rindt, C.C.M., 2009b. Characterization of MgSO_4 hydrate for thermochemical seasonal heat storage. *J. Sol. Energy Eng.* 131, 41014. <http://dx.doi.org/10.1115/1.4000275>.
- Whiting, G.T., Grondin, D., Stosic, D., Bennici, S., Auroux, A., 2014. Zeolite- MgCl_2 composites as potential long-term heat storage materials: influence of zeolite properties on heats of water sorption. *Sol. Energy Mater. Sol. Cells* 128, 289–295. <http://dx.doi.org/10.1016/j.solmat.2014.05.016>.
- Wu, H., Wang, S., Zhu, D., 2007. Effects of impregnating variables on dynamic sorption characteristics and storage properties of composite sorbent for solar heat storage. *Sol. Energy* 81, 864–871. <http://dx.doi.org/10.1016/j.solener.2006.11.013>.
- Ye, H., Yuan, Z., Li, S., Zhang, L., 2013. Activated carbon fiber cloth and CaCl_2 composite sorbents for a water vapor sorption cooling system. *Appl. Therm. Eng.* 61, 690–696. <http://dx.doi.org/10.1016/j.applthermaleng.2013.09.001>.
- Zheng, X., Ge, T.S., Wang, R.Z., Hu, L.M., 2014. Performance study of composite silica gels with different pore sizes and different impregnating hygroscopic salts. *Chem. Eng. Sci.* 120, 1–9. <http://dx.doi.org/10.1016/j.ces.2014.08.047>.
- Zhu, D., Wu, H., Wang, S., 2006. Experimental study on composite silica gel supported CaCl_2 sorbent for low grade heat storage. *Int. J. Therm. Sci.* 45, 804–813. <http://dx.doi.org/10.1016/j.ijthermalsci.2005.10.009>.
- Zondag, H., Kikkert, B., Smeding, S., de Boer, R., Bakker, M., 2013. Prototype thermochemical heat storage with open reactor system. *Appl. Energy* 109, 360–365. <http://dx.doi.org/10.1016/j.apenergy.2013.01.082>.