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Unexplored synthetic approaches for $CaCl_2$ impregnation for thermal energy storage

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Encapsulation of inorganic salt hydrates for thermal energy storage has been extensively researched. The application of composites in the form of shape-stabilized thermochemical change materials has been investigated as a potential remedy for the shortcomings of inorganic salt hydrates, including their low thermal conductivity and unstable nature. Several studies have investigated the application of porous matrices impregnated with calcium chloride for various applications, such as desiccant rotary wheels in dehumidification systems or thermal energy storage. The objective of this study was to determine the morphological and thermogravimetric effects of the three distinct impregnation techniques used: dry, wet and airbrush. Water uptake is comparable among the three samples produced by the various impregnation techniques, according to the results. The wet method yields a sample with a slightly greater surface area compared to the other two, attributed to a better dispersion of the salt throughout the matrix. In conclusion, the sample produced via dry impregnation exhibits the best solution when applied to large-scale production.

Keywords: silica gel, salt hydrates, impregnation, thermal storage capacity

Introduction

The impregnation of silica gel with salt hydrates is a crucial process for various applications, particularly in thermal energy storage and sorption studies(Casey et al., 2014) . This process consists in the segregation of a salt hydrate into the porous structure of silica gel (Zhang et al., 2023) to create a composite material, that offers several advantages, including increased thermal storage density and higher thermal stability (Huang et al., 2020).. Furthermore, the impregnation of silica gel with salt hydrates has been shown to address challenges such as low viscosity and leakage problems associated with the pure salt hydrates, thereby enhancing their applicability in thermal energy storage systems (Rajagopalan et al., 2022). In this study, three different techniques of impregnation were considered: dry, wet, and airbrush, in order to evaluate the influence between the three methods.

Materials and Method

Silica gel in the shape of spheres (average grain size 0.779 mm) with a surface area of 366.30 m^2/g and a pore volume of 1.049 cc/g, calcium chloride dihydrate and water for analysis were purchased from Sigma-Aldrich.

Firstly, the silica gel and the calcium chloride were dehydrated in oven at 120°C overnight. Following that, the salt was dissolved in varying volumes of water, in accordance with the impregnation method that was employed.

Table 1 - Samples obtained.

Sample Code	Approach	$\%CaCl_2$ (w/w)	$H_2O/CaCl_2$ (w/w)
CaCl30SG_DRY	Dry	30.0	2.2
CaCl30SG_WET	Wet	30.0	3.6
CaCl30SG_AB	Airbrush	30.0	3.6

In the Table 1, the percentages of the different preparations are detailed.

Dry impregnation, wet impregnation, and airbrush impregnation were the three used approaches. In the dry method a lower amount of water was used to dissolve the salt than the wet one. In both cases, impregnation involved dropping the solution into the matrix while stirring.

For airbrush impregnation, the same volume of water was utilised as for the wet method. In this case, an airbrush pen, with a 0.2 mm diameter needle, was used. The pen was placed vertically and was connected to a compressor that supplied airflow at a pressure of 3 bar. The saline solution was nebulized into a beaker containing the silica gel.

All the obtained samples were left overnight in oven preheated at 120°C. Surface area, water sorption/desorption capacities, and thermal storage capacity were analysed for each sample produced. The morphology of pure silica gel and impregnated materials was evaluated by an optical digital microscope.

Specific surface area and pore volume were measured using NOVA 1200e, Quantachrome Instruments. BET and BJH approaches were applied for the data analysis. The thermal storage capacity was measured through a customized thermogravimetric apparatus (Themys One, Setaram) with an evaporator and a vacuum system. Initially, the sample was dehydrated under vacuum (10^{-2} mbar) at a temperature of 120°C for 3 hours. The thermal storage capacity was evaluated under isobar conditions at 17 mbar (evaporation temperature of 15°C) within the cooling process from 120 °C to 25 °C with a scan rate of 5°C/min.

The evaluation of the composite materials hydration and dehydration capacities was carried out by DVS Vacuum, a thermo-gravimetric dynamic vapour system built by Surface Measurements Systems. The instrumental setup consists of a micro-balance (precision 0.1 µg) and a water vapor pressure flow control system inside the sample holder chamber.

Results and Discussion

With all the three impregnation methods, the calcium chloride was embedded within the pores of silica gel, as shown in Figure 1. Specifically, regarding airbrush impregnation, the salt has generated a shell that covers the matrix, resulting in a slight enlargement of its dimensions.

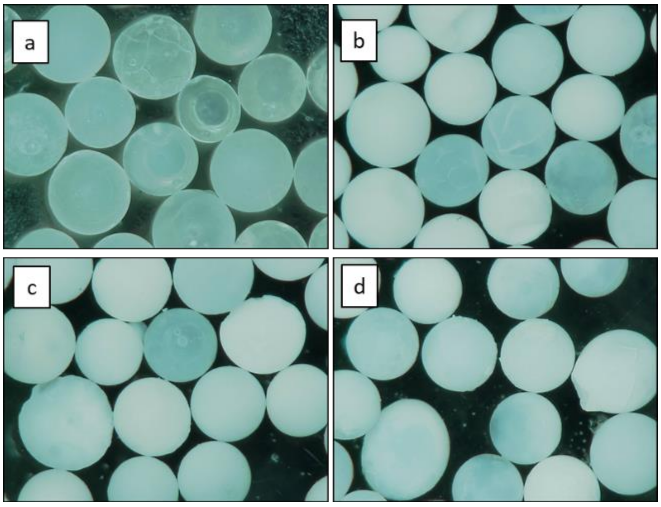

Figure 1 - Optical image of a) pure silica gel, b) CaCl30SG_DRY, c) CaCl30SG_WET and d) CaCl30SG_AB.

Furthermore, it is evident that all the synthetic approaches do not damage the matrix.

Table 2 shows the values of surface area compared to the silica gel. The materials obtained via dry and airbrush methods have a similar surface area, while that prepared with wet impregnation is slightly higher. This could be associated with the variation in water quantities used for the different impregnation techniques. The higher the salt solution, the higher is the capillary effect. Nevertheless, despite employing an equivalent volume of water, in both the wet and airbrush techniques, the nebulization doesn't permit full permeation into silica gel.

Table 2- Surface area results.

Sample Code	Surface area (m^2/g)
Silica Gel	**386.30**
CaCl30SG_DRY	**186.34**
CaCl30SG_WET	**197.88**
CaCl30SG_AB	**183.88**

Based on the thermogravimetric analysis of the data displayed in Figure 2, it is evident that the mass of the silica gel impregnated using the dry, wet, and airbrush methods varies by 44.07%, 47%, and 46.10%, respectively, as a result of water vapour absorption. Dry impregnation was observed to have a higher thermal storage capacity compared to the other two methods, which exhibited minimal differences.

The curves obtained from the DVS analysis (isobars at 17 mbar, 23 mbar and 31 mbar) confirm the trend of the thermogravimetric analysis, where the CaCl30SG_WET sample appears to absorb a greater quantity of water than the other two samples.

Furthermore, a slight local hysteresis cycle was observed on all the samples made at a temperature of 50°C and 75°C (Figure 3). This behavior is clearly associated with the change in the hydration level of calcium chloride (Van Essen et al., 2009).

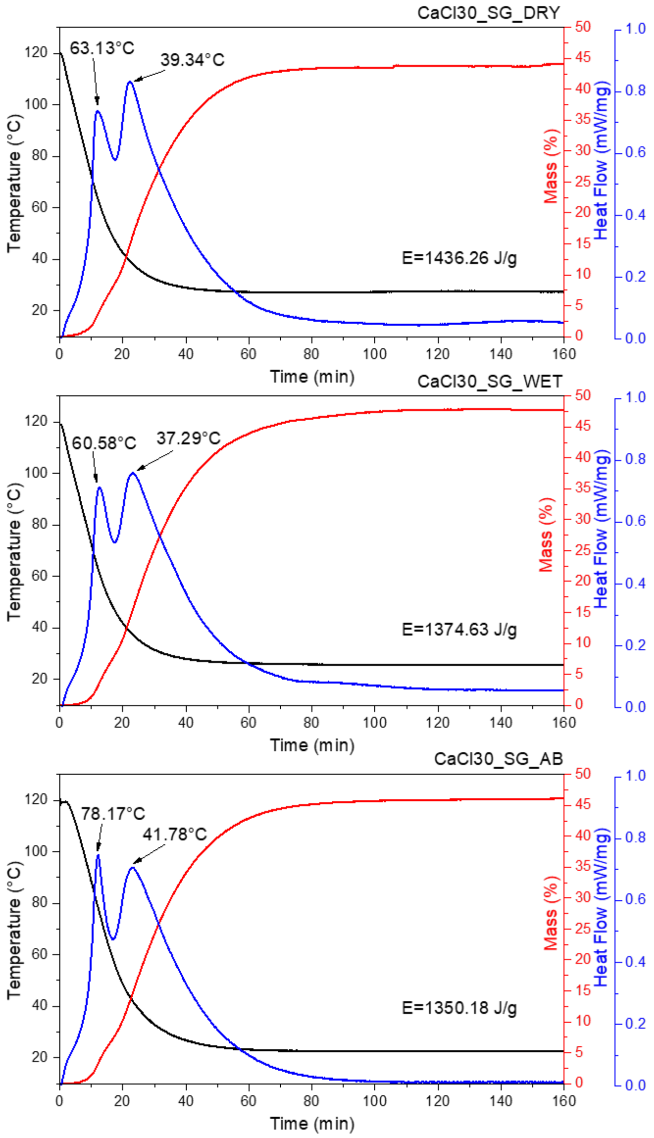

Figure 2 – Results of thermogravimetric analysis

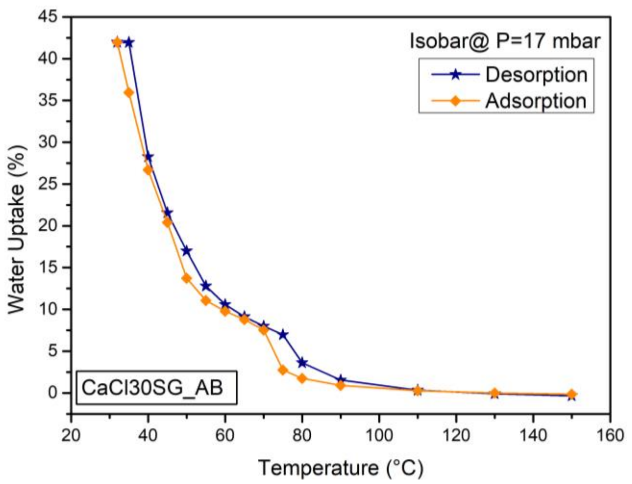

Figure 3 - Isobar (P=17 mbar) of CaCl30SG_AB

Conclusion

In this study we investigated how the performance of composite materials for thermal storage varies, using three different impregnation methodologies (dry, wet and airbrush). In terms of water uptake, the three samples present similar performances. However, the sample obtained with the wet approach shows a slightly higher surface area than the other two, due to a better dispersion of the salt within the matrix. The isobars obtained from the DVS analysis reveal a minor hysteresis between the absorption and desorption curves for all three samples. In conclusion, based on these preliminary data, the sample produced by dry impregnation appears to be the most effective for large scale production.

Acknowledgment

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