ENERSTOCK 2024
The 16th IAE EST CP International Conference on Energy Storage
June 5–7, 2024
Lyon, France

Experimental assessment of inorganic salts impregnated silica gel matrix for thermal energy storage applications.

A. Fotia[1,*], E. Mastronardo[1], V. Brancato[2], C. Milone[1] A. Frazzica[2], L. Calabrese[1],
1 University of Messina, Department of Engineering, Contrada di Dio, 98165 Messina, Italy
2 CNR - Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", Via Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy
*Corresponding author e-mail: antonio.fotia@unime.it

The state of the art in thermal energy storage has seen significant advancements with the incorporation of inorganic salts impregnated in different matrices. These matrices have shown promise in addressing the limitations of this kind of material, particularly in terms of reducing deliquescence. In this study, silica gel was examined as a matrix that was impregnated with three different inorganic salts: calcium chloride, magnesium chloride and magnesium sulphate. Deliquescence observation were carried out via optical microscopy. Thermogravimetric analyses in static and dynamic vapor conditions, , were performed in order to extrapolate the water uptake and enthalpy values of the different samples. The results obtained show that the CaCl30SG sample appears to be the best performing in terms of enthalpy and water uptake. Unfortunately, the sample containing calcium chloride exhibited a significantly greater degree of deliquescence than the other two samples analysed. Hence, a promising candidate could be considered MgSO30SG which enables lower deliquescence with still a high storage capacity.

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

Introduction

Thermal energy storage (TES) systems have gained significant attention in order to efficiently store and utilize thermal energy for various applications, including solar power plants, electronic devices, photovoltaic modules, and Li-ion battery systems (Arshad et al., 2020). These systems rely on the use of heat storage materials, such as inorganic salts, to store and release thermal energy. In particular, inorganic salt have garnered significant attention due to their high latent heat of fusion, cost-effectiveness, and high volumetric energy storage density (Xie et al., 2017). The solid-state hydration of salts, such as salt hydrates, has been particularly emphasized in the context of TES (Sögütoglu et al., 2019) .Furthermore, salt hydrates, have attracted attention due to their reasonable price, wide sources, good thermal conductivity, and high volumetric energy storage density (Jing et al., 2023)In fact, inorganic salt hydrates, such as calcium chloride hexahydrate (CaCl2•6H2O), have been utilized in solar energy heating and building materials owing to their suitable phase-change temperature and high thermal storage capacity (Zhang et al., 2018). However, inorganic salts have certain drawbacks, such as phase separation and supercooling, which limit their applicability in thermal energy storage systems (Tao et al., 2020). To overcome these challenges, researchers have turned to impregnating inorganic salts into various matrices to enhance their chemical and thermal stability.

Materials and Method

Silica gel in the shape of spheres (average grain size 0.779 mm), magnesium chloride anhydrous, calcium chloride dihydrate, magnesium sulphate heptahydrate and water for analysis were purchased from Sigma-Aldrich. All the materials used were at first dehydrated in oven at 120°C overnight.

The three analyzed samples were obtained by impregnating silica gel with an aqueous solution containing dissolved salt. The composites thus obtained are composed of 30% salt and 70% silica gel.

Table 1 - Batches prepared.

Sample Code	Salt	Matrix	%Salt
CaCl30SG	$CaCl_2$	Silica gel	30.0
MgCl30SG	$MgCl_2$	Silica gel	30.0
MgSO30SG	$MgSO_4$	Silica gel	30.0

The morphology and deliquescence of the materials were evaluated by a digital optical microscope. The images obtained (Figure 1) show the samples, dry and after one hour of exposure to a relative humidity of 60% and a temperature of 26.5°C.

The DVS Vacuum a thermogravimetric dynamic vapour system (manufactured by Surface Measurements Systems, Ltd., Alperton, UK), was employed to evaluate the composite materials' hydration and dehydration capabilities. The apparatus configuration comprises a 0.1 µg precise microbalance and a control system that regulates the flow of water vapour pressure within the sample holder's chamber. The water vapour pressures used for the experiments are 8.65, 12.24, and 17 mbar.

A specialized thermogravimetric static apparatus (Themys One, Setaram) equipped with an evaporator and a vacuum system conducted the assessment of thermal storage capacity. The procedure began with vacuum dehydration of the sample at a temperature of 120°C for a duration of 3 hours (under a vacuum pressure of 10-2 mbar). Subsequently, the thermal storage capacity was measured under isobaric conditions at 17 mbar (evaporation temperature of 15°C). This evaluation was performed during the cooling process, ranging from 120°C to 25°C, with a scanning rate of 5°C/min.

Results and Discussion

The images obtained (Figure 1) through the optical microscope highlight a marked deliquescence in the silica gel impregnated with calcium chloride (visually identifiable by the acquired transparency in the particles) after one hour exposed in a controlled atmosphere (r.h.=60%, T=26.5°C). The other two batches, impregnated with magnesium chloride and magnesium sulphate, prove to be more stable and do not show deliquescence after exposure in the humid environment.

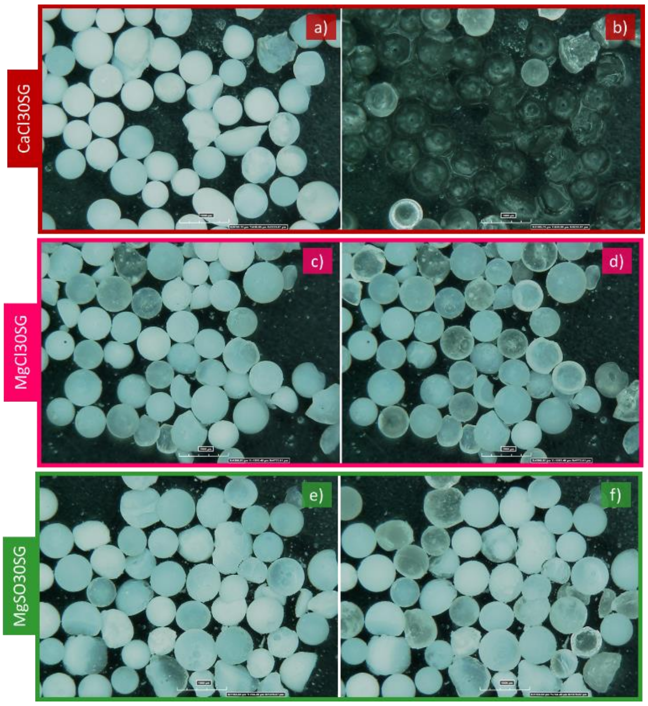

Figure 1 - Comparison of optical microscope images of dried samples a), c) and e), and after one hour exposed in a controlled atmosphere b), d), and f).

Further information can be argued evaluating the trend of water vapour sorption isobars in the range of *temperature* *30-150°C* (

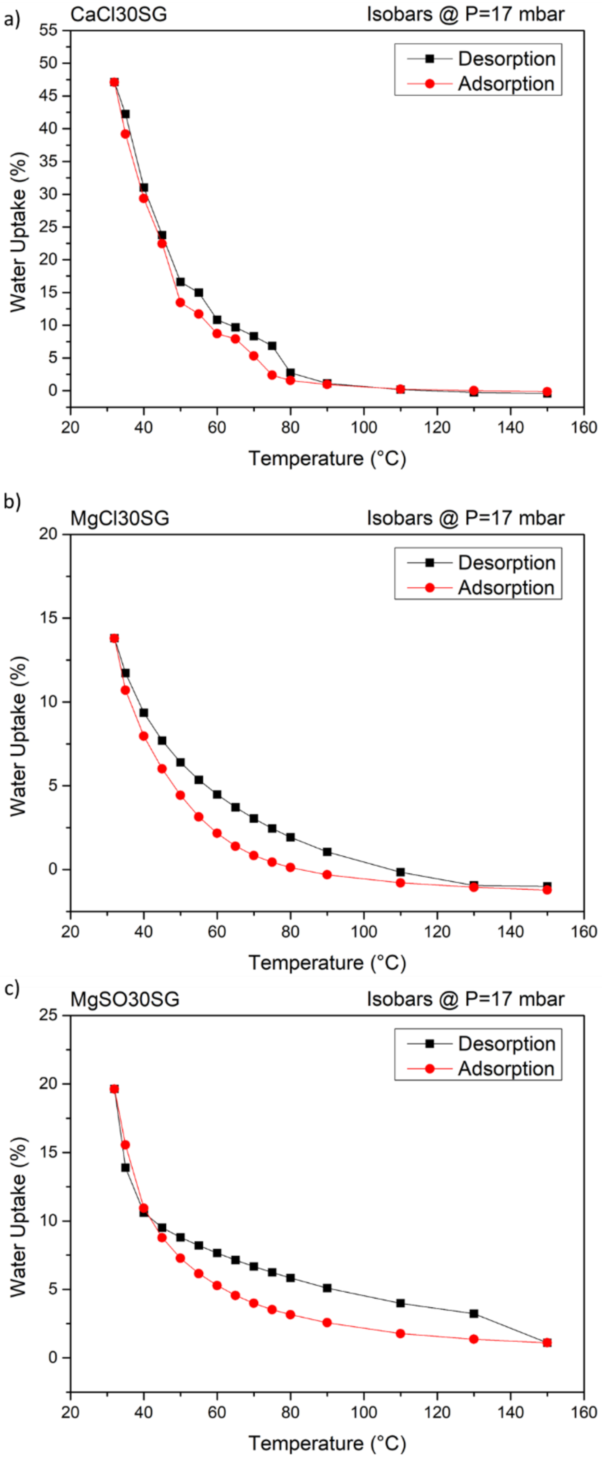

Figure 2).

The different shapes of the isobars obtained from the DVS analysis depend on the salts used for impregnation. For brevity, only the curves relating to a vapour pressure equal to 17mbar have been represented. In the case of the MgCl30SG and MgSO30SG samples, the curves present an exponential-type trend. While analysing the shape of the curve relating to the CaCl30SG sample, we can notice two steps corresponding to the temperatures of 50°C and 75°C. These two steps are due to phases in which the calcium chloride is stable at a certain level of hydration (Van Essen et al., 2009). For all three samples, the hysteresis phenomenon decreases as the water vapour pressure increases.

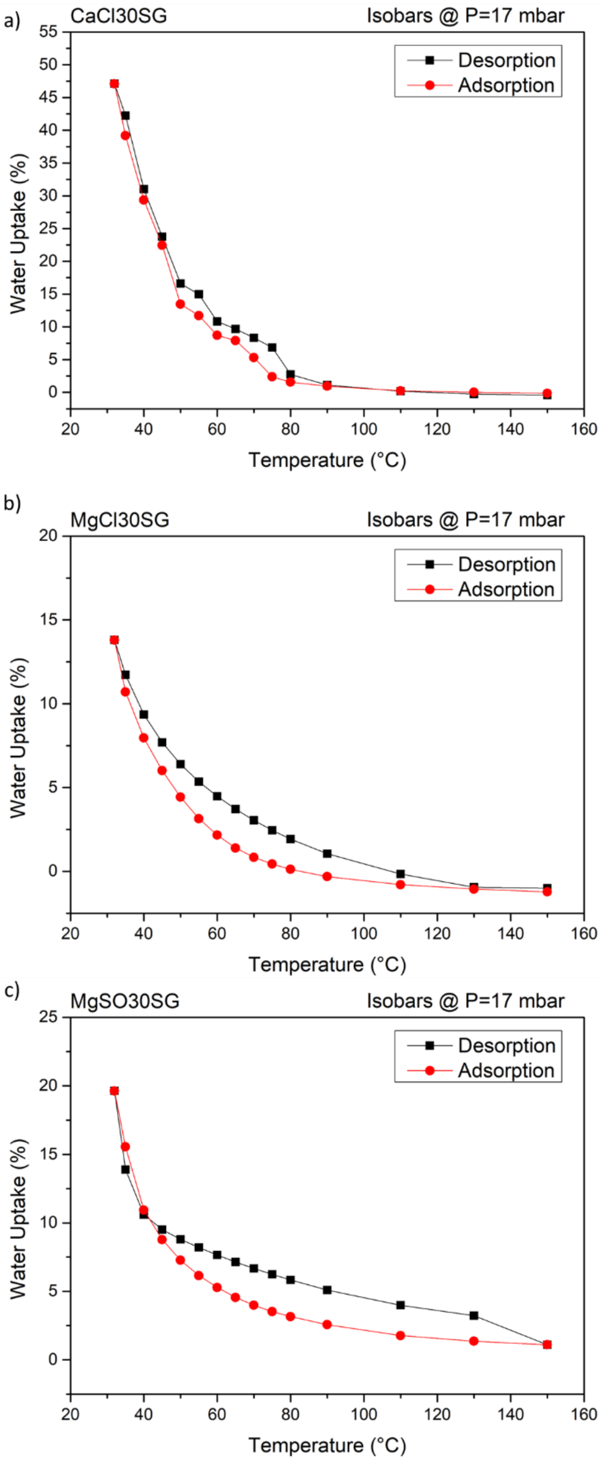

Figure 2 – Water vapor sorption isobars of a) CaCl30SG, b) MgCl30SG and c) MgSO30SG.

Figure 4 shows the water uptake and enthalpy values. These values were extrapolated from thermogravimetric analyses (Figure 3), identifying the maximum water uptake for each batch (occurring at the lowest applied temperature equal to 30°C). Both values relative to the sample impregnated with calcium chloride are greater than those of the other two samples. In fact, for the CaCl30SG sample it has a water uptake of 47.77% compared to 23.93% and 26.72% for the MgCl30SG and MgSO30SG. Consequently, the sample containing calcium chloride possesses an enthalpy of 1374.63 J/g, whereas the samples containing magnesium chloride and magnesium sulphate have enthalpy values 44.50% (763.04 J/g) and 30.13% (960.51 J/g) lower than CaCl30SG batch, respectively. The enthalpy values were calculated through the time-dependent integration of the heat flow curve.

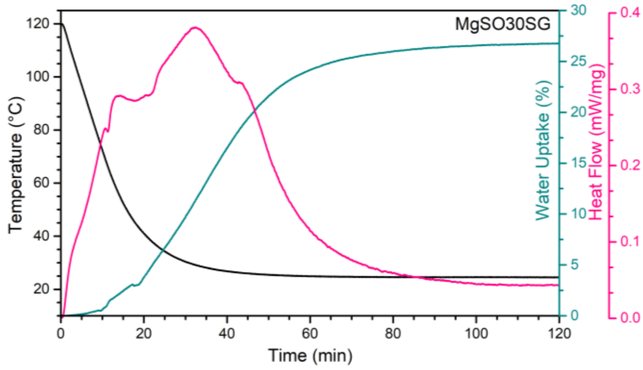

Figure 3 - Results of static thermogravimetric analysis relative of MgSO30SG.

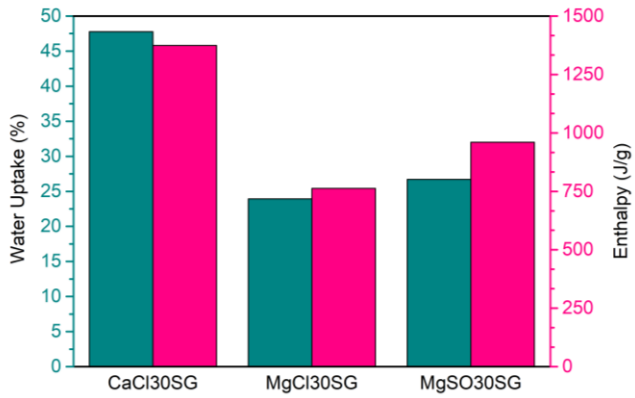

Figure 4 - Comparison between the water uptake and enthalpy values of the different samples.

Conclusion

In conclusion, from the study of the results obtained, the CaCl30SG sample appears to be the best performing in terms of enthalpy and water uptake. Unfortunately, the sample containing calcium chloride exhibited a significantly greater degree of deliquescence than the other two samples analysed.

Acknowledgment

This project has received funding from ThumbsUp (Thermal energy storage solUtions to optimally Manage BuildingS and Unlock their grid balancing and flexibility Potential).ThumbsUP is a Horizon Europe Project supported by the European Commission under contract No. 101096921.

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