

# Sorption Test Bench for Zeolite and Salt-Composite Based Thermochemical Storage

Gayaneh Issayan<sup>1</sup> and Bernhard Zettl<sup>1</sup>

<sup>1</sup> University of Applied Sciences Upper Austria, Wels (Austria)

## Abstract

The advancements in thermochemical storage technologies benefit strongly from a holistic research approach ranging from material and component development to demonstration applications. This work presents a sorption test bench developed and constructed to evaluate thermochemical materials, such as zeolites and salt-hydrate composites, in 0.01-1.0 kg batches and under fully controlled conditions. The test bench is utilized for thermogravimetric state of charge (SOC) determination of open sorption prototypes. Further, the influence of salt-hydrate mixtures on the sorption behavior of salt-composites were studied. The results on outlet storage temperatures for zeolite and salt-composite beds are presented in this work.

*Keywords: thermochemical storage, sorption test bench, salt-hydrate composites, zeolites, SOC, thermogravimetry*

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## 1. Introduction

The urgency of a global shift to renewable energies and CO<sub>2</sub> reduction motivates energy storage and efficiency research efforts. Thermal energy storages (TES) impact multiple sectors of the renewable energy transition, such as sector coupling, improving grid resilience, and industrial processing. Thermochemical storages are based on the ability of thermochemical materials (TCM) to store energy without noticeable losses during the conservation phase through sorption processes or chemical reactions. Thermochemical storages can act as long-term storage to overcome the seasonal solar mismatch and regenerate waste heat. Although TCMs, such as zeolites, silica gels, metal-organic frameworks (MOFs), etc., are accounted for high theoretical energy densities and sufficient temperature rise on the material level, the demonstration applications have not redeemed themselves financially or energetically (Zettl, 2019). Low-cost salt-hydrates and various composites based on salt in matrix design have also been investigated to show disadvantages, such as poor stability towards cycling, insufficient temperature increase, low deliquescence, etc. (Lin et al., 2021, Scapino, 2017). As previously reported, salt-hydrate and natural zeolite composites have been developed in form of shape stable granules and pellets (Issayan et al., 2021). Consequently, a designated thermogravimetric setup was constructed suitable for the characterization of the latter composites in larger batches (10-50g) in both closed and open system settings (Issayan, Zettl, 2022a). The focus of current TCM studies is the influence of salt-hydrate mixtures on sorption behavior and cycling stability of composites (Katyal, 2020, Xueling et al., 2021). The preliminary results on chloride salts of magnesium, lithium, and calcium from latter thermogravimetric setup were reported (Issayan, Zettl, 2022b). The promising samples were then selected to be further investigated in larger batches.

In this work, a lab-scale (kilogram range), multi-mode (fluidized and fixed bed) open sorption test bench was developed to conduct a thermogravimetric state-of-charge determination of salt-containing composite storage materials. The results from a fixed bed storage simulation model were utilized to validate the results from the test bench for the common 13X BF (binder-free) zeolite bed, which will then act as a benchmark for further analysis of the composite material performance. This work presents the preliminary results of thermogravimetric investigations of various salt-hydrate containing TCMs in two different reactor constellations.

## 2. Methods and materials

### 2.1 Experimental setup

The realization of the open sorption systems differs mainly in implementation of the reactor bed design. Three

main reactor beds are shown in Fig. 1. The open sorption setup was developed to conduct thermogravimetric analysis of thermochemical storage materials, mainly zeolites in fixed bed reactors. For salt-containing composites the setup was upgraded to also enable experiments in fluidized bed settings. The adsorption of water molecules in porous zeolites is limited by the pore volume and subsequently shows a natural saturation behavior when the pores fill up. In contrast to zeolites, the water molecules are incorporated into the crystal structure of the salts. If more water molecules are available, the salts “overhydrate” until a gel-like or dissolved layer forms, which prevents further absorption. For this reason, in fixed bed reactors a reaction front is formed, and the overhydrated layers prevent the optimal mass flow through the bed. Hence, fluidized bed measurements with smaller amounts of material and higher mass flows were also implemented.

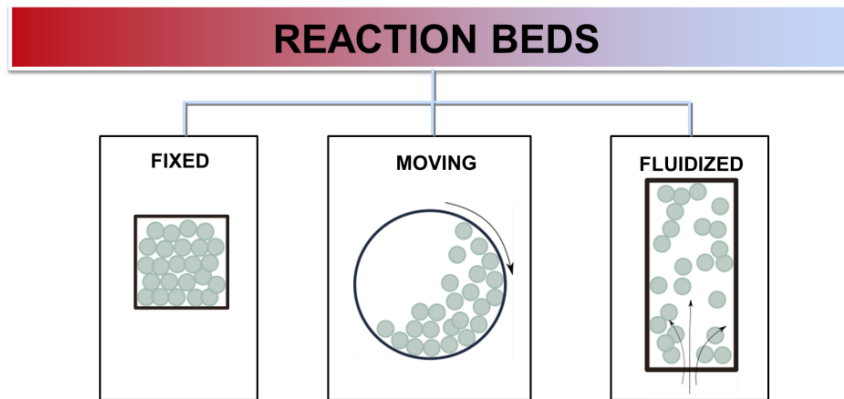


Fig. 1: Three main types of sorption reactor beds utilized in thermal storage applications.

A schematic sketch of the setup is presented in Fig. 2 and consists of analytical mass balance, heating element, fogger with the corresponding tank, and centrifugal blower. The fogger unit enables the generation of airflow with controlled humidity from ambient up to 90% relative humidity (RH). The heater itself can reach up to 300°C resulting in input air mass up to 250°C at the bed. The material is placed in a cylindrical glass container on the balance, where the temperature, humidity, and mass flow of the output air can be monitored. The containers vary in size, housing from 0.01 kg up to 1.0 kg material and can be equipped with further temperature sensors to record the temperatures in various positions of the bed. The three input parameters, temperature, humidity, and mass flow, are controlled individually, allowing for fixed-point measurements and programmed ramps and routines for cycling.

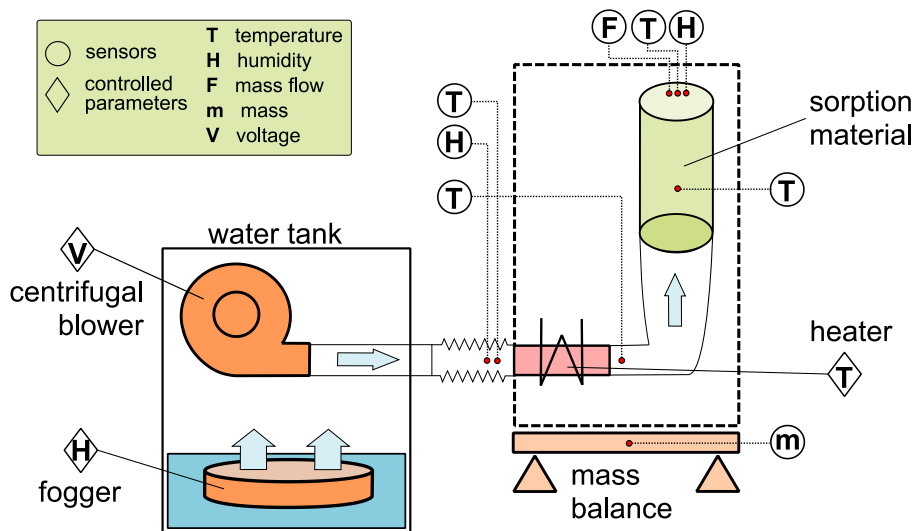


Fig. 2: Schematic representation of the sorption test bench including sensors and controlled parameters.

## 2.2 Materials

The reference synthetic zeolite 13X binder-free was purchased from CWK (Chemiewerk Bad Kösteritz) in two granule sizes and used with two different regeneration temperatures (see Tab. 1). As the study of salt-hydrate

mixtures was the focus of this work, salt-in-matrix composition was used to prepare simple composites and ease the handling of the samples during the experiments. Therefore, natural zeolite, clinoptilolite, was used as the porous matrix and was impregnated with magnesium, lithium and calcium chloride ( $MgCl_2$ ,  $LiCl$ ,  $CaCl_2$ ). The salt-hydrates were purchased in anhydrous state with high purity. Saturated solutions of the mixtures of different salt fractions were prepared and impregnated in clinoptilolite, which was sieved in fine ( $40 \mu m - 1 mm$ ) and coarse ( $1mm - 3 mm$ ) granularity. The accumulated salt on the outer grain-surface of the dried samples were then washed out with water, which otherwise caused premature overhydration of the samples. Lastly, the samples were dried at  $110^\circ C$ . The sample names and detailed compositions of prepared samples are summarized in following Tab. 1.

Tab. 1 Prepared samples and their composition

Name	Composition	Desorption temperature
13XBF-small 13XBF-large	1.5 – 2.5 mm granules -> cycled 2.5 – 5.0 mm granules -> new purchase	$200^\circ C$ $250^\circ C$
CaLi-15 CaLi-20	fine clino + 15wt.% -> $CaCl_2:LiCl - 50:50$ fine clino + 20wt.% -> $CaCl_2:LiCl - 50:50$	$110^\circ C$
MgLi-55f MgLi-82 MgLi-28 MgLi-55c	fine clino + 15wt.% -> $MgCl_2:LiCl - 50:50$ fine clino + 15wt.% -> $MgCl_2:LiCl - 80:20$ fine clino + 15wt.% -> $MgCl_2:LiCl - 20:80$ coarse clino + 15wt.% -> $MgCl_2:LiCl - 50:50$	$110^\circ C$

### 3. Results and discussion

#### 3.1 Reference zeolite

As previously mentioned, a numerical model of fixed bed open sorption system based on linear driving force model was used to validate the results from the test bench (Daborer-Prado et al., 2022). The simulation was conducted with material data of well-studied and demonstrated 13XBF zeolites. The model implementation was done in MATLAB®/Simulink. The results obtained from the simulation model were compared to the measurement results and validated the utilized methods.

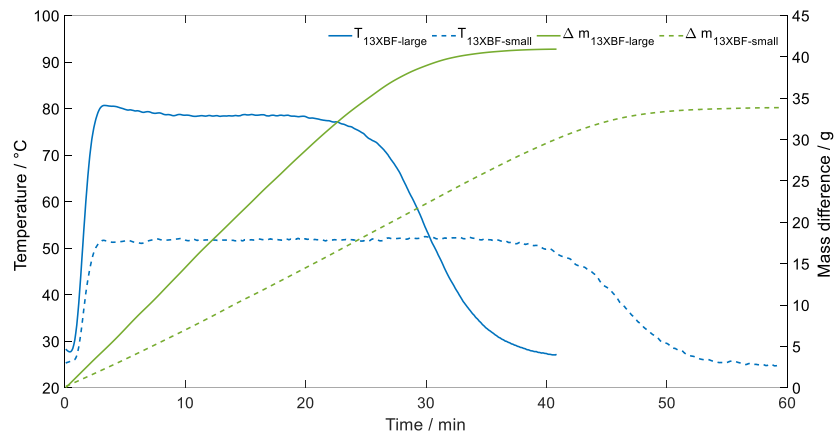


Fig. 3: Two measurements of zeolite 13XBF of different granule diameters and regeneration temperatures.

Two exemplary zeolite measurements are presented in this work. The experiments were conducted by varying the inlet mass flow and relative humidity of the air and recording the temperature and mass change of the sorption bed during adsorption. The material used for the experiments weighed 150 g. The experimental temperature outputs (blue lines) and mass change results (green lines) for an inlet air with 70% RH at  $25^\circ C$  and mass flow values of  $4 kg/h$  are presented in Fig. 3. The solid lines represent larger granules, which allow better mass flow

through the sorption bed and were regenerated at 250°C. The dashed lines correspond to smaller granules, which have been cycled multiple times in experimental settings and regenerated at 200°C. The temperature levels achieved by the larger granules are distinctly higher, than those coming from the smaller ones. However, the high temperature plateau does only last about 30 minutes. Possible degradations in the pore structure of the smaller and often cycled granules could be the reason for the moderate to low temperature levels, which then last for 45 – 50 min. The green lines, which correspond to the mass gained by the material at the given conditions show saturation behavior appropriate to the temperature output. The 13XBF-small sample adsorbs 22.6 wt.% and 13XBF-large adsorbs 27.3 wt.%. According to product data sheets (water vapor - isotherms) both samples exhibit a maximum water saturation of over 30 wt.%. Apart from discrepancies attributed to heat losses, material qualities and measurement artifacts, the experimental results gained from the test bench agreed well with the previous measurements.

### 3.2 Salt-composites in fluidized bed

The test bench was mainly utilized to evaluate the temperature response of salt-containing composites in comparable settings. Due to CaCl<sub>2</sub> low deliquescence humidity, the salt is able to absorb water vapor in ambient conditions and tends to overhydration (Rammelberg et al., 2012). The sorption capacity and stability of CaCl<sub>2</sub> was shown to strongly benefit from addition of LiCl (Issayan, Zettl, 2022a). The latter pair was selected for the first fluidized bed measurements. One of the pressing issues regarding the impregnation was the salt content, as clinoptilolite has shown limited sorption capacity of around 5 – 10wt.%. Therefore, the air flow deploying 60% RH at 25°C was set in such way, that 50g of material was fluidized. The temperature profiles were obtained from samples with varying salt content CaLi-15 and CaLi-20 and are presented in Fig. 4. The sample with higher salt content did not show benefits regarding the temperature output, as well as the CaLi-15 sample, which was tested using more humid air flow (65%RH). Best results were obtained by using low humidity mass flow. Summarizing, the measurements on CaCl<sub>2</sub>-LiCl mixtures were not satisfactory, as the temperature levels sank rapidly and overhydration of the samples could be observed.

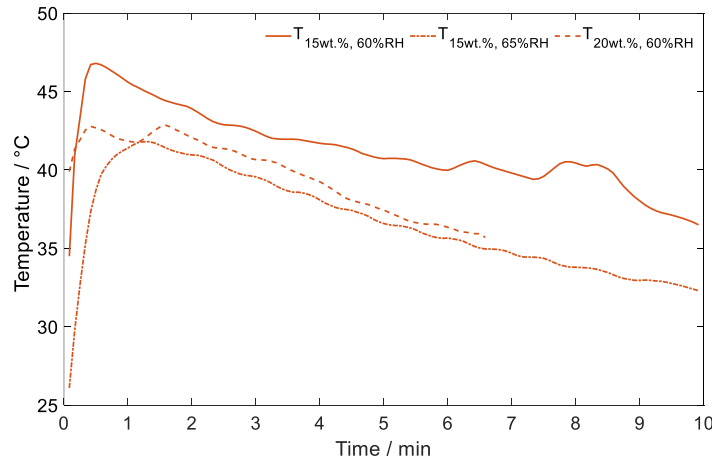


Fig. 4: CaLi-15 sample with 15wt.% salt content tested in fluidized bed with 60 and 65% RH (solid and dash-dotted lines) and compared to the sample with 20wt.% salt CaLi-20.

One of the well-studied salt-hydrates in thermochemical storage material context is MgCl<sub>2</sub> (Rammelberg et al., 2012). The MgLi-55f samples weighing 75 g were also tested using two humidity levels in fluidized bed setting and the results are depicted in Fig. 5. The highest temperature from the salt-composites is achieved at the beginning, after a steep rise, followed by a steady decrease. The higher the relative humidity of the air flow, the faster the material reaction and the higher the temperature response of the bed. The consequence of higher humidity is the faster decrease of the temperature. The temperature output was comparable to those of CaCl<sub>2</sub>-LiCl mixtures. However, the sample was stable and did not show signs of overhydration, which will be further discussed in scope of fixed bed measurements. Beside the temperature, the mass increase is also presented as the green lines and shows a steady increase appropriate to the temperature response. The overall mass gains of 8 wt.% and 9.3 wt.% can almost entirely be attributed to salt-hydrates (< 15 wt.%).

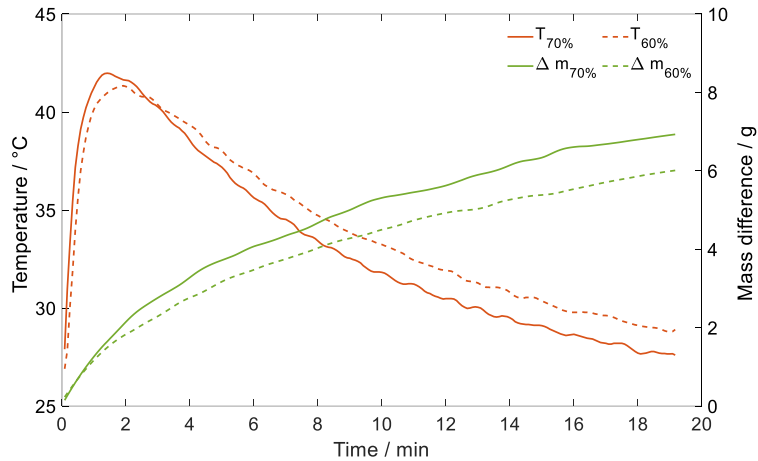


Fig. 5: MgLi-55f in fluidized bed setting and varying humidity.

### 3.3 Salt-composites in fixed bed

Fixed bed measurements were performed by using the same input parameters as for the zeolite measurements: 4 kg/h air flow with 70% RH at 25°C. In all measurements material bed weighted 150 g.

The results of fixed bed measurements of composites with varying granule sizes are presented in Fig. 6. The mass flow through the coarse composite bed caused the rapid temperature response slightly below 60°C, which drastically fell after the first 2 – 3 minutes. As the coarse samples have lower surface to volume ratio, it was not possible for the salts to penetrate the deeper pores. Therefore, the salt accumulations near the surface quickly overhydrated during the measurements. In comparison, the composites with fine granularity deploy the first high temperature level after around 5 min and hold temperatures above 55°C for further 20 minutes.

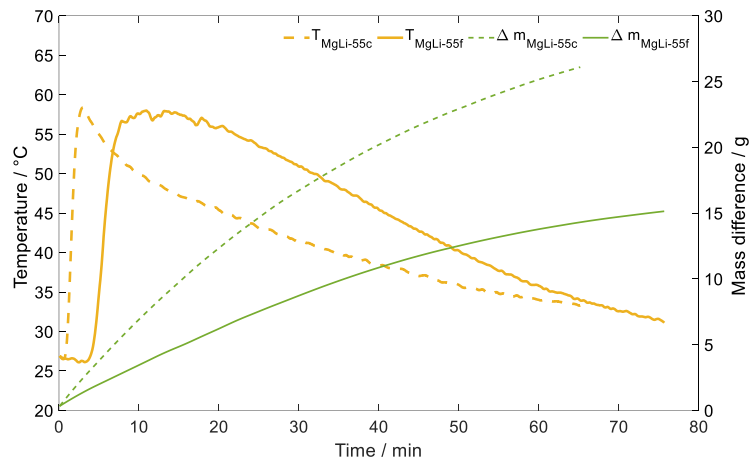


Fig. 6: Comparison of coarse and fine granular composites with MgCl<sub>2</sub>-LiCl impregnation.

Adsorption data of MgCl<sub>2</sub>-LiCl samples impregnated in microporous vermiculite were reported and have shown interesting trends (Issayan, Zettl, 2022b). Hence the motivation to investigate some of well-performing samples in the test bench. The adsorption data presented in Fig. 7 was collected in a closed vacuum chamber reported in (Issayan, Zettl, 2022b), where the samples were exposed to low partial pressures (10 mbar). The sorbent temperature inside the vacuum chamber and the normalized loading related to the initial mass of the sample are displayed on the left and right y-axes, respectively. The solid lines represent the sample with 50/50 weight ratio of MgCl<sub>2</sub>-LiCl-mixture (~MgLi-55). The dashed lines correspond to 20/80 (~MgLi-28) and the dah-dotted lines to MgCl<sub>2</sub>-LiCl-mixture (~MgLi-82). Clinoptilolite composites with the mentioned mixture ratio were prepared and measured in the test bench to study and compare the behavior of salt-mixtures in low-content composites and open and fixed bed storage setting versus those measured in closed vacuum chamber shown in Fig. 7. The results

of three  $\text{MgCl}_2$ -LiCl-mixtures are presented in Fig. 8. The line styles and sample names of the samples with the same ratio are kept similar to those in Fig. 7.

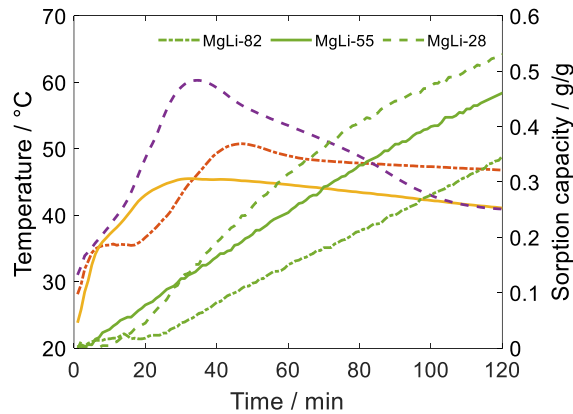


Fig. 7: Adsorption behavior of the  $\text{MgCl}_2$ -LiCl samples in vacuum chamber (Issayan, Zettl, 2022b).

After the first 30 minutes, MgLi-28 sample in Fig. 7 (vacuum chamber) reaches the highest temperature, which was attributed to the LiCl, as it performs the best in closed systems. MgLi-55 sample shows the lowest temperature increase. MgLi-82 sample has shown the moderate temperature increase. However, the temperature levels held for the longest duration. The adsorption process was decelerated for MgLi-82 sample. In fixed bed setting in Fig. 8, the latter mixture (red dashed line) achieved and held temperatures around 50°C in the first hour. The temperature output from MgLi-28 was the lowest yet held the longest. In both cases strong overhydration of the samples could be observed, which should be addressed in composite development phase of the future work. Hence, the only sample, which achieved temperatures over 50°C and showed stable behavior in fixed bed setting was the MgLi-55f sample. The temperature levels were held significantly shorter in comparison with those from other  $\text{MgCl}_2$ -LiCl ratios. The highest mass gain was registered for MgLi-28. The sorption capacities of all the samples in the vacuum chamber (Fig. 7) after eight hours are in the same order of magnitude: MgLi-55 ~0.9 g/g, MgLi-82 ~ 0.85 g/g and MgLi-28 ~ 1.0 g/g. Therefore, we can conclude that salt-hydrates absorb/adsorb roughly their initial mass. The samples in Fig. 8 show an increase in mass around 10 – 16 wt.%, which also corresponds to the salt-content impregnated in clinoptilolite.

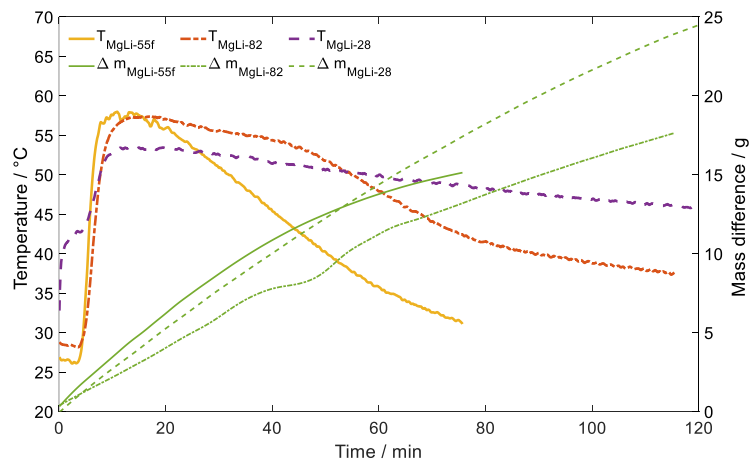


Fig. 8: Comparison of samples with different  $\text{MgCl}_2$  to LiCl ratios.

#### 4. Conclusion and outlook

The results from the test bench point out interesting characteristics of salt-composites and motivate further work in this field. The fluidized bed concept was implemented, which enabled the investigation of humidity sensitive samples. Steps will be taken to improve the setup and continuously increase the batch size of the material. Despite

the challenges with overhydration and poor mass flow through dense beds, fixed bed measurements delivered interesting and motivating insights. Considering the small amount of salt-hydrate in the composites and the low regeneration/desorption temperatures compared to the zeolites, all three samples from the MgCl<sub>2</sub>-LiCl series showed promising temperature outputs. The samples MgLi-82 and MgLi-28 should be further stabilized regarding overhydration. Only the 50/50 mixture of MgCl<sub>2</sub>-LiCl (sample MgLi-55f) was stable and did not overhydrate during the measurements.

Further goals are to develop stabilized composites using binders and fibers. The investigation of further salt-hydrate mixtures is also an ongoing work. The test bench was found to be appropriate for measurements on salt-containing materials and will be equipped to perform calorimetric measurements.

## 5. Acknowledgments

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## 6. References

- Daborer-Prado, N., Issayan, G., Zettl, B., 2022. Experimental validation of a solid sorption mathematical model. In Conference of Environmental and Climate Technologies (Connect 2022). Riga, Latvia. Environmental and Climate Technologies 26, no 1, pp 377-391. [10.2478/rtuect-2022-0029](https://doi.org/10.2478/rtuect-2022-0029)
- Issayan, G., Zettl, B., Somitsch, W., 2021. Developing and stabilizing salt-hydrate composites as thermal storage materials. In 14th International Renewable Energy Storage Conference 2020 (IRES 2020). Atlantis Press. p. 49-57. [10.2991/ahc.k.210202.008](https://doi.org/10.2991/ahc.k.210202.008)
- Issayan, G., Zettl, B., 2022a. Novel thermogravimetric characterization method for adsorption cycles of TCM. In 15th International Renewable Energy Storage Conference 2021 (IRES 2021). Atlantis Press. p. 108-117. [10.2991/ahc.k.220301.011](https://doi.org/10.2991/ahc.k.220301.011)
- Issayan, G., Zettl, B., 2022b. Investigation of salt-mixtures for thermochemical material development. In 2<sup>nd</sup> International Sustainable Energy Conference (ISEC 2022), Graz, Austria. [10.32638/isec2022](https://doi.org/10.32638/isec2022)
- Katyal, S., 2020. Experimental assessment of mixed salt hydrates for thermochemical storage. Master thesis, University of Eindhoven. Available at: [https://pure.tue.nl/ws/portalfiles/portal/165891380/1282018\\_Master\\_Thesis\\_Report\\_Katyal.pdf](https://pure.tue.nl/ws/portalfiles/portal/165891380/1282018_Master_Thesis_Report_Katyal.pdf) (Accessed: 12 September 2022).
- Lin, J., Zhao, Q., Huang, H., Mao, H., Liu, Y., Xiao, Y., 2021. Applications of low-temperature thermochemical energy storage systems for salt hydrates based on material classification: A Review. Solar Energy 214, p. 149-178. [10.1016/j.solener.2020.11.055](https://doi.org/10.1016/j.solener.2020.11.055)
- Rammelberg, H. U., Schmidt, T. and Ruck, W., 2012. Hydration and dehydration of salt hydrates and hydroxides for thermal energy storage – kinetics and energy release. Energy. Proced. 30, p. 362-369. [10.1016/j.egypro.2012.11.043](https://doi.org/10.1016/j.egypro.2012.11.043)
- Scapino, L., Zondag, H. A., Van Bael, J., Diriken, J., Rindt, C. C., 2017. Sorption heat storage for long-term low-temperature applications: A review on the advancements at material and prototype scale. Appl. Energy. 190, 920-948. [10.1016/j.apenergy.2016.12.148](https://doi.org/10.1016/j.apenergy.2016.12.148)
- Xueling, Z., Feifei, W., Qi, Z., Xudong, L., Yanling, W., Yejiang, Z., Chuanxiao, C., Tingxiang, J., 2021. Heat storage performance analysis of ZMS-Porous media/CaCl<sub>2</sub>/MgSO<sub>4</sub> composite thermochemical heat storage materials. Solar Energy Materials and Solar Cells, 230, 111246. [10.1016/j.solmat.2021.111246](https://doi.org/10.1016/j.solmat.2021.111246)
- Zettl, B., 2019. Long-term thermochemical heat storage for low-temperature applications. Proceedings of Solar World Congress SWC, 4.-7.11 2019, Santiago, CHILE. [10.18086/swc.2019.08.11](https://doi.org/10.18086/swc.2019.08.11)