EuroSun 2026

LAB-SCALE REACTOR FOR CHARACTERIZATION OF THERMOCHEMICAL HEAT STORAGE USING SALT HYDRATE MATERIALS

Summary

This study presents the design and validation of a lab-scale reactor engineered to bridge the gap between micro-scale material research and industrial-scale thermochemical heat storage. By monitoring temperature, humidity, and mass fluctuations, the designed system characterizes the hydration kinetics of salt hydrates like $CaCl_2$. Preliminary results highlight how macro-scale phenomena, such as volumetric expansion, significantly influence water intake rates and reaction advancement. Consequently, these insights will inform the geometric optimization of the components and the development of mitigation strategies for future large-scale prototypes.

Keywords: Thermochemical Heat Storage, Salt Hydrates, Reaction Kinetics, Lab-scale Reactor, Calcium Chloride.

Field of application for the findings: Thermal Energy Storage for integration of renewable energy sources or industrial waste heat.

Addressed audience: Researchers in thermochemical heat storage, energy systems engineers, and industrial developers working on sustainable heating solutions.

1. Introduction

The transition to sustainable, decarbonized energy requires integrating renewable sources, yet their intermittency creates a temporal mismatch with building heating demands. Thermal Energy Storage (TES) bridges this gap, with Thermochemical Heat Storage (TCS) standing out for its high energy density and minimal thermal losses during long-term storage [5]. Salt hydrates are particularly promising for domestic heating, as their reversible hydration reactions (as presented in Equation 1) align with temperatures from solar thermal collectors and industrial waste heat [4].

$$Salt \cdot \alpha H_2O(s) + (\beta - \alpha)H_2O(g) \underset{\text{dehydration}}{\overset{\text{hydration}}{\rightleftharpoons}} Salt \cdot \beta H_2O(s) + Heat \tag{1}$$

However, a gap persists between fundamental research and commercialization. Conventional micro-scale characterization, such as Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) [3], utilizes milligram-scale samples that fail to capture critical macro-scale phenomena like intra-bed heat and mass transfer resistances, particle agglomeration, deliquescence, and volumetric expansion.

Because full-scale prototype testing is cost-prohibitive and complex, intermediate lab-scale platforms are essential. This study presents the design and validation of an integrated reaction system engineered to evaluate bulk material behavior, cyclic stability, and transport dynamics, providing a robust bridge toward industrial-scale implementation.

2. Methods and approach

The reactor is configured to evaluate reaction performance based on the degree of reaction advancement, enabling a comparative analysis with the data obtained by the TGA and DSC measurements [2]. By identifying empirical deviations, specific hypotheses regarding the transport phenomena and kinetic inhibitors affecting the process can be formulated.

Reaction advancement is tracked via multiple integrated mechanisms. Primarily, high-precision humidity and temperature sensors (SHT35 - ComWinTop), positioned at the reactor inlet and outlet, facilitate the measurement of differential vapor concentration, as depicted in Figure 1; this serves as a metric for the moisture uptake or release within the reactive bed. These data enable the derivation of reaction rates and the characterization of reactant transformation kinetics over time. Concurrently, the reactor is integrated into a dynamic gravimetric monitoring system to record real-time mass fluctuations during the hydration and

dehydration cycles. Furthermore, an array of thermocouples is distributed longitudinally and radially inside the reactor to profile the thermal behavior of the process. Experiments were conducted under standardized conditions: an ambient temperature of 19°C and 100 g of initially anhydrous $CaCl_2$. The process relative humidity was modulated to achieve specific hydration states by adjusting the mixing ratio of dry and water-saturated air within the humidification unit.

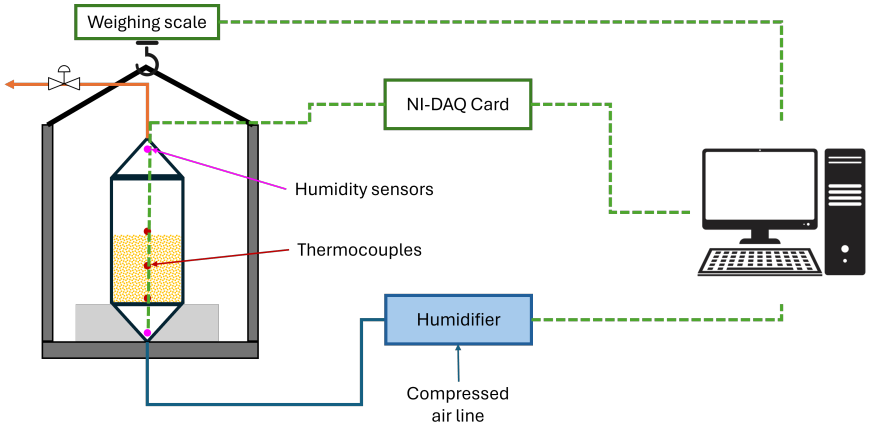

Fig. 1: Schematic layout of the experimental setup for monitoring thermochemical reaction kinetics. The system integrates three primary diagnostic functionalities to track reaction advancement: gravimetric analysis, thermal profiling, and hygrometric monitoring.

3. Preliminary results

The hydration process was evaluated to calibrate the operational parameters of the humidification unit. Guided by the study of Wang et al. [6], the system was configured to supply an air stream at 10% RH at an ambient temperature of approximately 20 °C, targeting the formation of calcium chloride tetrahydrate ($CaCl_2{\cdot}4H_2O$). This setpoint was selected to ensure sufficient exothermic energy for sensor detection while avoiding the formation of hexahydrate structures, which are susceptible to deliquescence, thereby causing agglomeration and blockage inside the reactor. To ensure reproducibility, the experiment was conducted in triplicate using a distinct batch of high-purity $CaCl_2$ for each iteration. The results, illustrated in Figure 2, demonstrate high stability in the feed conditions at the reactor inlet. The consistent profiles observed across all three experiments for both temperature and relative humidity gradients (inlet vs. outlet) confirm the reliability of the control methodology.

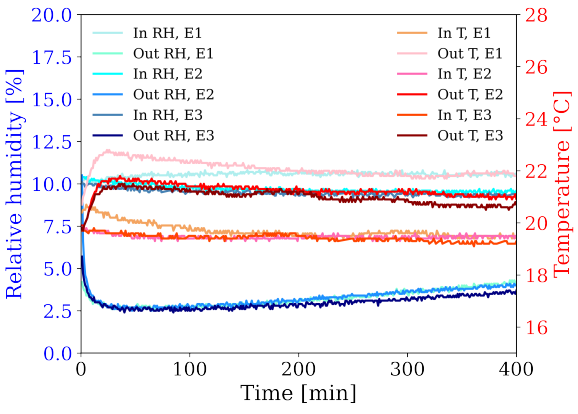

Fig. 2: Temperature and humidity profiles at the reactor inlet and outlet during the hydration of anhydrous $CaCl_2$ at 10% RH for method characterization.

To further characterize material behavior, operational conditions were adjusted to facilitate the formation of hexahydrate crystals ($CaCl_2{\cdot}6H_2O$), thereby magnifying potential inhibitory effects within the bed. According to literature [6], this state is achievable at 18% RH at room temperature. A comparative analysis, presented in Figure 3 A), reveals contrasting kinetic trends between the two hydration states. While the tetrahydration reaction exhibits a lower, yet more uniform, rate of water uptake, the hexahydration process displays a distinctive two-phase behavior. This trend is further analyzed by computing the water intake rate, detailed in Figure 3 B),

where initially, a significant differential in water intake is observed, which rapidly diminishes before transitioning into a more stabilized second phase. This observation corroborates the hypothesis that macro-scale performance may be influenced by effects such as volume expansion and agglomeration. This phenomenon, intrinsically linked to the hydration level of the inorganic salt, reduces internal bed porosity and subsequently restricts the reactive surface area available to the working fluid.

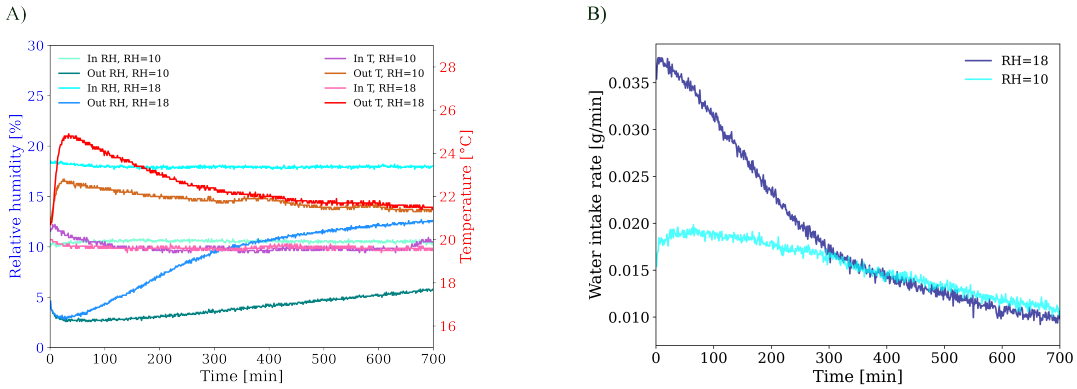

Fig. 3: A) Evolution of temperature and humidity profiles at the reactor inlet and outlet during the hydration of $CaCl_2$ at two different inlet RH: 10% and 18%, illustrating the formation of tetrahydrate and hexahydrate crystalline structures correspondingly. B) Water vapor intake rate as a function of time between the inlet and outlet streams.

4. Research outlook

Preliminary findings indicate that bulk material behavior deviates significantly from micro-scale observations. Consequently, further experimental validation is required to ensure direct control during material characterization. To complement the existing analytical capabilities of the reaction system, the integration of macrogravimetric analysis constitutes the critical next step. This enhancement will facilitate the empirical verification of reaction kinetics and the dynamic behavior of the reactive media, offering a more detailed observation of mass accumulation within the salt crystalline structures. Finally, to substantiate the preliminary conclusions derived from bulk bed behavior, the reactor will be equipped with a modular sample containment system. This device is engineered to maintain the structural integrity of the reacted material during transport to a Micro-CT [1] apparatus for high-resolution X-ray tomography. Such internal imaging will allow for the precise characterization of the geometric phase distributions and pore-scale morphological changes forecasted by the secondary analytical methods.

References

[1] Aastha Arya, Jorge Martinez-Garcia, Philipp Schuetz, Amirhoushang Mahmoudi, Gerrit Brem, Pim AJ Donkers, and Mina Shahi. Characterizing changes in a salt hydrate bed using micro x-ray computed tomography. *Journal of Nondestructive Evaluation*, 43(3):77, 2024.

[2] Margarethe Molenda, Jana Stengler, Marc Linder, and Antje Wörner. Reversible hydration behavior of cacl2 at high h2o partial pressures for thermochemical energy storage. *Thermochimica acta*, 560:76–81, 2013.

[3] O Opel, HU Rammelberg, M Gérard, and W Ruck. Thermochemical storage materials research-tga/dsc-hydration studies. In *Proceedings of the international conference for sustainable energy storage*, volume 24. Ulster Belfast, 2011.

[4] Tomasz Spietz, Rafał Fryza, Janusz Lasek, and Jarosław Zuwała. Thermochemical energy storage based on salt hydrates: A comprehensive review. *Energies*, 18(10):2643, 2025.

[5] Awash Tekle Tafere. Thermal energy storage technologies: A review of current landscape and future directions. *F1000Research*, 15:83, 2026.

[6] Shaoheng Wang, Amelie Stahlbuhk, and Michael Steiger. Hydration and deliquescence behavior of calcium chloride hydrates. *Fluid Phase Equilibria*, 585:114171, 2024.