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Thermochemical Energy Storage: an approach to integration pathways

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***Abstract*— In this work we test the potential of thermochemical energy storage (TCES) for waste-heat recovery in industry processes. Different TCES technologies were considered, finding sorption TCES the most promising. The temperature range of TCES sorption technologies is extensively wide, so this work focuses on the most unexplored range, 100-300 °C, which also fits the heat generated in several industry processes. The hydrate salt $MgCl_2$ was incorporated into alumina, obtaining a heat storage capacity >500 kJ/kg. Through the results from this work and follow-up studies, we will facilitate the industrial uptake of water-sorption thermochemical energy storage materials and technologies.**

Keywords*— *Thermochemical Energy Storage, Water Sorption, Thermal Energy Storage, Waste Heat Recovery.

I. Introduction

A. Thermal Energy Storage

On top of the already critical climate crisis, the current energy situation in Europe calls for a rapid change in European energy systems. In Norway, high electricity prices have led to increased focus on energy-saving and energy-storing technologies. The International Energy Agency [1] provides a series of main guidelines for a secure and environmentally friendly exit from the current energy crisis. Among them, it is imperative to upscale clean energy technologies and scale down fossil fuels. Since most renewable energy systems are volatile, developments and improvements of energy storage technologies are key to ensure sufficient flexibility and avoid fossil back-up.

Thermal energy storage (TES) can allow decoupling between supply and demand and could enable a significant reduction in global greenhouse gas emissions by reducing the need for fossil fuel back-up technologies and through increased utilization of waste heat. [2,3] Although there are some commercial options, many TES technologies are still in early development, and research is needed on short- to long-term alternatives for a wide range of operational temperatures, and to maximize energy storage capacity and compactness at the lowest price. [4,5,6] For TES to enable the transition from fossil fuels to renewable sources of energy, solutions that are tailormade for each application are necessary.

The concept of TES addresses the goal of **reduced energy consumption and CO_2 emissions** through several pathways: First; allowing for an increasing share of renewable and intermittent energy sources in the energy mix by decoupling energy production and consumption in time. Second; saving waste heat by providing a means of affordable decoupling of industrial excess heat and its utilization. This research also tackles some of the sustainable development goals of the United Nations by focusing on a clean energy (goal 7) for industry innovation (goal 9) that can contribute to create and improve more sustainable cities and communities (goal 11).

B. Market potential

More and more industry companies are expressing interest in TES implementation. For all of them, an integrated TES system would improve the flexibility and efficient usage of the heat system. If we consider addressing 10% of the yearly 20 TWh of industrial waste heat in Norway [7], with an average price of 30 kEUR/MWh (very large scale) and about 50 charge/discharge cycles per year, the total addressable market (TAM) in Norway adds up to €1.2 billion by 2030. UK company Infracapital, which invested €110 million in the Norwegian company EnergyNest in 2021 [8], evaluated the global market for TES technologies to €300+ billion by 2030, all temperature ranges included. In this context, an innovative concept, water-sorption thermochemical energy storage, has the potential of taking part of this market share, however also expanding the market to long-term (from days to weeks/months) storage where other TES options, such as phase change materials, would not be suited.

II. Overview of Thermochemical Energy Storage

A. Classification

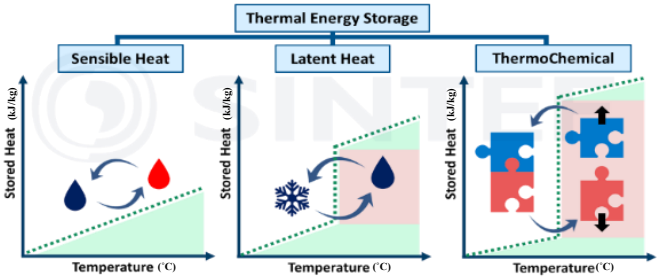

Fig. 1: Stored heat as function of temperature for different TES technologies.

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There are three main TES approaches depending on the physical/chemical properties of the employed materials. Depending on the behavior of the TES compounds with variations of temperature, the different technologies can be classified as sensible, latent, or thermochemical energy storage (see Fig. 1). [2]

While thermochemical energy storage (TCES) offers the highest capacity, power, and efficiency, it is also the most complex technology, and has currently the highest cost (see Table 1). [9] TCES has theoretically a high energy density with negligible heat losses, so it could be also considered for long-term energy storage in various applications (including heat storage from renewable sources and heat waste from industrial activities). [10,11,12]

TABLE 1: Comparison of sensible, latent, and thermochemical energy storage technologies. [9]

TES System	Capacity (kWh/t)	Power (MW)	Efficiency (%)	Cost (€/kWh)
Sensible	10-50	0.001-10.0	50-90	0.1-10
Latent	50-100	0.001-1.0	75-90	10-50
Thermochemical	120-250	0.01-1	75-100	8-100

Even though TCES is a promising technology, its complexity requires improvements before commercial integration in energy systems. [13] TCES is based on reversible chemical reactions and, depending on the type of the reactions, there are different TCES approaches. Firstly, TCES can be divided in sorption systems and chemical reactions. Sorption technologies include adsorption, absorption, or both, and entails fixation or capture of gas or vapor by a sorbent. [14] Chemical reactions can be divided into solid-gas and solid-liquid processes and involve a change in the molecular configuration of the compounds involved. [15]

B. Water-sorption TCES

Of the TCES methods, water-sorption is the most promising and feasible system due to its relatively easy operation, high reliability, and safety compared to others such as carbon dioxide or ammonia sorption. Water-sorption processes require cheap, abundant, and non-toxic materials that interact with water as sorption/desorption source. [16] Another attractive characteristic is the temperature range, which can encompass the range from room temperature up to 300 °C. [17] The chemical process (see Fig. 2) consists of two steps:

- Charge: Dehydration of the hydrated compound takes place with a heat source at a high temperature. In this process the material absorbs heat from the environment while releasing water. It will remain charged as long as it is kept dehydrated. [18]
- Discharge: at low temperature, when exposed to a humid atmosphere, the material is hydrated, releasing the stored energy in the process. [18]

The properties of a TCES system depend mainly on the properties of the sorption material. The main properties to look at are energy storage density of the sorption process, charge/discharge temperatures, chemical and mechanical stability, toxicity, thermal conductivity, heat capacity, and price. [19, 20] The order of selection criteria is case dependent, with key target to ensure a high heat storage capacity, good cyclability, efficient heat transfer and safety at the lowest cost. [21,22]

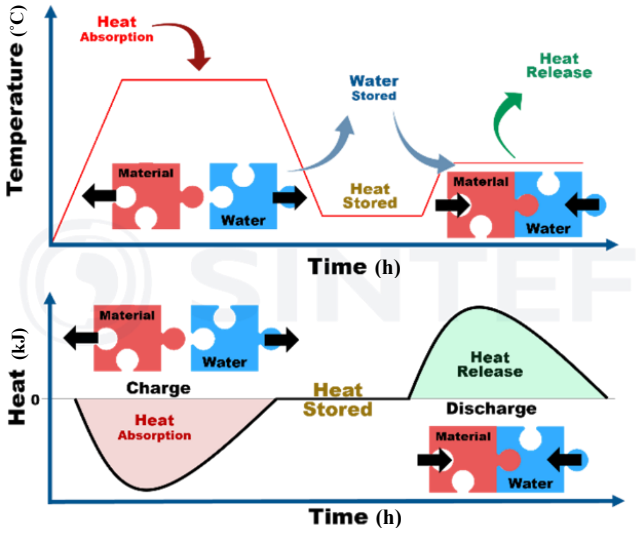

Fig. 2: Description of water-sorption TCES with temperatures of the processes and heat absorbed/released as a function of time.

Salt hydrates are the most studied materials for water-sorption TCES given that they have the potential to cover all the requirements mentioned before; however, the TRL is still low (3-4) due to implementation challenges involving the conformation of the materials (to avoid phenomena as agglomeration of the hydrated form or low heat and mass transfer), structure and device stability control to achieve optimal performance. [23] For this work, we have selected the hydrated salt of $MgCl_2$, which has been studied for water sorption TCES. [24] $MgCl_2$ presents dehydration reactions around 100˚C, so it is a suitable candidate to store waste heat. [23]

One of the strategies to improve the performance of hydrated salts is to impregnate them in a porous matrix [23] that allows the enhancement of the sorption power (by increasing the surface) and avoids the agglomeration of the hydrated form. In the case of $MgCl_2$, there are examples using zeolite as porous media [24] for water sorption and it has also been studied for ammonia sorption using alumina as porous media [25]. In this context, we decided to study the impregnation in alumina for water sorption, which has not been studied in much detail before despite alumina being a simpler and cheaper compound comparing to zeolite.

III. Objectives

At SINTEF Energy Research, we are working on water sorption TCES through the project ITChES (Integration of ThermoChemical Energy Storage), together with SINTEF Industry, within the framework of the Centre for Environment-friendly Energy Research FME HighEff.

The main objective is to facilitate the industrial uptake of water- sorption thermochemical energy storage materials and technologies by analyzing the performance potential of compounds able to recover excess heat.

Through lab scale characterization of selected materials, we aim to overcome the crucial next step towards industrial use by performance analysis of candidate materials under relevant conditions at lab scale and study the path for further upscaling

and integration. One advantage of TCES is the potential for economic upscaling, as storage tanks and recirculation rate of the material can be easily upscaled to enable an improved heat storage capacity without big modifications in the reactor (the costly part).

IV. Methodology and Experimental Results

A. Methodology

5.00g of $MgCl_2 \cdot 6H_2O$ (99-102%, ACS) were dissolved in 2.2mL of H_2O and added to 4.00 g of alumina (high surface area, ThermoScientific). The impregnated pellets were dried at 125˚C and then grinded manually and left for 72h in a saturated wet atmosphere. The final mass ratio was approximate 1:1 of Al_2O_3:$MgCl_2 \cdot 6H_2O$, however further analysis will be conducted in the future with other characterization techniques to establish a more accurate composition. 64.32mg of the composite were measured in a Netzsch STA Thermal Analyser with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). A dehydration study was performed dynamically from 25 to 130˚C at a heating rate of 5K/min followed by an isotherm at 130˚C for 20 minutes.

B. Results and discussion

Fig. 3 shows the TGA and DSC results. Looking at the TGA, there is a mass loss of 30% due to the dehydration.
The preparation of the composite requires drying it at 125˚C, so we consider that step as the first dehydration cycle of $MgCl_2 \cdot 6H_2O$. After that, during the 72h of hydration, the $MgCl_2$ is hydrated again (between 25˚C and 50˚C according to literature) [26]. The TGA-DSC measurements are run on that sample, so the results correspond to the second dehydration cycle, confirming the reversibility of the process.

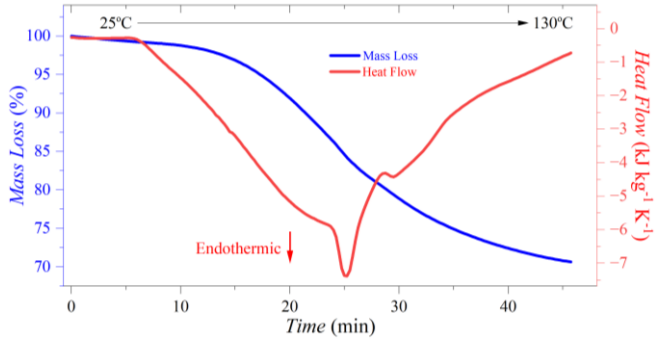

Fig. 3: Mass loss (blue) and heat flow (red) of the composite Al_2O_3 - $MgCl_2 \cdot 6H_2O$ as function of time from 25˚ to 130˚C. The red arrow indicates that the heat flow signal is endothermic.

Regarding the DSC, there are at least 3 visible events. The first one, at 15 min (corresponding to ~55˚C) is the dehydration of $MgCl_2 \cdot 6H_2O$ to $MgCl_2 \cdot 5H_2O$. The last event at 30 min (corresponding to ~120˚C) is the dehydration of $MgCl_2 \cdot 5H_2O$ to $MgCl_2 \cdot 4H_2O$. The largest heat adsorption at 25 min (~100˚C) is the evaporation of the hydrated water. It is not clear if all the evaporated water corresponds to the dehydrated water from the $MgCl_2$ or if there is also water absorbed by the alumina. This will be further studied.
By integrating the heat flow signal as function of time, we obtained a value of 530 kJ/kg for the heat storage capacity of the composite (see Fig. 4). This value is higher with that recently reported for a similar composite of zeolite - $MgCl_2 \cdot 6H_2O$, which presents ~417 kJ/kg in the same temperature range. [27] Compared to the latent heat storage capacity of latent and sensible heat storage systems using water [28] (the most common), the here reported composite Al_2O_3:$MgCl_2$ shows a considerably higher value, as shown in Fig. 4.

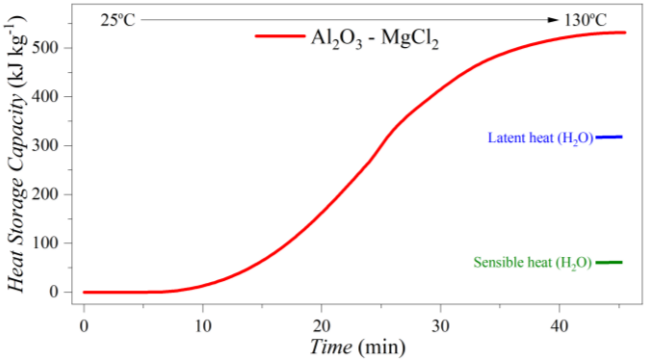

Fig. 4: Heat storage capacity of the composite Al_2O_3 - $MgCl_2 \cdot 6H_2O$ as function of time. The heat storage capacity for water as phase change material (melting/solidification) and as sensible heat storage medium in the same temperature interval (without considering the evaporation) are shown in blue and green, respectively.

V. Conclusions

In this work, we present the results of characterization of the composite Al_2O_3:$MgCl_2$ for water-sorption thermochemical energy storage. This composite, studied before only as potential material for ammonia-sorption, can offer some advantages with respect to others using zeolite as matrix, which is a more complex and expensive material than alumina. The obtained heat storage capacity (540 kJ/kg) is higher than other TES systems such as PCMs or water tanks, highlighting the potential of water-sorption TCES to become the most attractive TES technology.
However, there is still a gap between the materials research and the development of how to improve their performance in the conditions of real processes, and this is due to the complexity of the required reactors and the lack of studies on the materials in a relevant environment. And that is precisely the next step of this research, studying the performance of the Al_2O_3:$MgCl_2$ composite in a fluidized bed reactor.
Water-sorption TCES is a promising technology with great potential for waste heat recovery. The extensive investigation of TCES materials, such as this work, reveals that there are materials with great potential as candidates for the technology, but there is still a lack of studies analysing their performance in reactors. That is the key enabler for upscaling and integration, and it will be the continuation of this work, bringing water-sorption TCES closer to its integration for the end user.

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