TECHNISCHE UNIVERSITÄT WIEN

DIPLOMARBEIT – MASTER THESIS

Thermochemical heat storage for motor vehicles – practical analysis of heat storage materials for application in motor vehicles

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Chemische Wärmespeicherung für Kraftfahrzeuge - Praktische Analyse von Wärmespeichermaterialien für den Einsatz im KFZ

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines
Diplom-Ingenieurs unter der Leitung von

Assoc. Prof. Dr. techn. Peter Hofmann

und

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Aufgabenstellung für die Diplomarbeit

Conceptual formulation

Herrn Ulrich Maximilian, Matrikelnummer: 09 26 470 wird folgende Aufgabe gestellt:

„Chemische Wärmespeicherung für Kraftfahrzeuge - Praktische Analyse von Wärmespeichermaterialien für den Einsatz im KFZ“

Es ist eine praktische Analyse von Wärmespeichermaterialien für den Einsatz im KFZ durchzuführen.

Schwerpunkte:

- Literaturrecherche
- Vorfeldrecherche bezüglich thermochemischer Wärmespeichermaterialien zur Verwendung in Kombination mit Trägermaterialien (Glasfaser) und Treffen einer Vorauswahl von geeigneten Wärmespeichermaterialien zur Anwendung in Kraftfahrzeugen.
- Adaption und Inbetriebnahme eines Versuchsstands zur Analyse thermochemischer Speichermaterialien.
- Praktische Prüfung der Materialien in einem Versuchsreaktor. Untersuchungen hinsichtlich Speichertemperatur, Wärmemenge und Reaktionskinetik.
- Bewertung/Diskussion der Ergebnisse im Rahmen der Diplomarbeit

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Preface

This master thesis was created during my time as a graduand at the Institute for Powertrains and Automotive Technology (IFA) at the Technical University of Vienna, Austria during the project “Wärmespeicherung III”, funded by the Research Association for Combustion Engines (FVV) eV.

Particular gratitude goes to Associate Prof. Dipl.-Ing. Dr.techn. Peter Hofmann as primary supervisor of this master thesis and Projektass. Dipl.-Ing. Fabian Havlik, BSc as co-supervisor. Further I thank all staff members of IFA for providing help and advice.

I dedicate this work to my parents who made it possible for me to achieve this goal, thank you.

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Abstract

In an effort to further decrease fuel consumption of motor vehicles, to meet increasingly stricter environmental standards, the use of previously unused or partially used heat flows gains increased focus. A possibility to use otherwise unused heat flows, could be by storing unused heat until it can be put to use. Thermochemical storage has the potential to effectively store heat over time and allow for previously unused heat to be used when additional heat is sought after. Cold start and warmup phases of motor vehicles pose working conditions where additional heat can be used in a beneficial way.

Thermochemical heat storage (TCHS) is a potentially promising candidate because of its ability to store heat without heat loss due to thermal conductivity or thermal radiation, enabling long-term storage without thermal insulation.

The Goal of this work was to test different thermochemical heat storage materials for their applicability in combination with a carrier material, to form a thermochemical heat storage composite for use in motor vehicles.

Further, a compact TCHS system was manufactured to test TCHS composites and evaluate the feasibility of a modular TCHS system, consisting of independent and compact storage devices at feasible motor vehicle locations.

Kurzfassung

Mit dem Bestreben den Kraftstoffverbrauch von Kraftfahrzeugen weiter zu senken, um immer strikter werdenden Umweltstandards gerecht zu werden, rücken ungenutzte bzw. nur teilweise genutzte Wärmeströme in den Fokus. Eine Möglichkeit der Nutzung, der ansonsten ungenützten Wärme, besteht in der Speicherung der Wärme, bis eine sinnvolle Nutzung möglich ist. Thermochemische Wärmespeicherung bietet das Potential Wärme effizient zu speichern und erlaubt die Nutzung von bisher ungenutzter Wärme, wenn zusätzliche Wärme gefragt ist. Kaltstart und Warmlaufphase des Kraftfahrzeugs stellen Arbeitsbedingungen dar in denen zusätzliche Wärme vorteilhaft genutzt werden kann.

Thermochemische Wärmespeicherung ist ein potentiell vielversprechender Ansatz, wegen der Fähigkeit Wärme ohne Wärmeverlust aufgrund von Wärmeleitung oder Wärmestrahlung zu speichern. Dies ermöglicht Langzeitspeicherung von Wärme ohne thermische Isolation.

Ziel dieser Arbeit war die Untersuchung verschiedener thermochemischer Wärmespeichermaterialien auf deren Eignung, in Kombination mit einem Trägermaterial, ein Komposit zur thermochemischen Wärmespeicherung für den Einsatz in Fahrzeugen zu bilden. Des Weiteren, wurde ein Prototyp eines kompakten thermochemischen Wärmespeichers, sowohl für die Evaluierung von TCHS-Kompositen erstellt, als auch um die Machbarkeit eines modularen Wärmespeichers zu testen. Dieses modulare Konzept sieht vor, voneinander unabhängige kompakte Wärmespeicher, an dafür praktikablen Stellen eines Kraftfahrzeugs zu implementieren.

List of abbreviations

$Al_2(SO_4)_3$	Aluminium sulphate
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
D	Debye, CGS (not SI) unit of the electric dipole moment)
DSC	differential scanning calorimetry
(g)	Gaseous state
GHG	Greenhouse gas
HCl	Hydrogen chloride
H_2O	Water
LiBr	Lithium bromide
$MgCl_2$	Magnesium chloride
$MgSO_4$	Magnesium sulphate
NEDC	New European driving cycle
Q	Heat storage capacity
(s)	Solid state
TCHS	Thermochemical heat storage

1 Introduction

1.1 Motivation for the implementation of thermochemical heat storage in motor vehicles

Climate change poses one of the major threats of the civilised world. In order to reduce or stop effects of climate change, greenhouse gas (GHG) emissions have to be reduced. Motor vehicles, mostly powered by internal combustion engines, present one of the major sources of GHG emissions. In order to stimulate reduction of GHG emissions, governments pass increasingly stricter emissions standards in order to fulfil international agreements on reduction of GHG emissions. Those stricter emission standards include limiting the maximum emissions of CO_2 to 95 g/km for overall fleet consumption in 2020, real driving emissions tests or a possible future Euro 7 emissions standard. [1], [2], [3]

Cold start and warm up phases are very inefficient operation phases (high oil viscosity and colder combustion temperature than normal due to higher thermal losses through the cylinder walls) for internal combustion engines, therefore the reduction/shortening of cold start and warmup phases is key, in order to reduce additional fuel used during these stages.

Heat storage, the ability to store excess heat (during normal operation) and reuse it when needed (during cold start respectively warmup) can lead to a shorter warmup phase of the engine and therefore reduced fuel consumption during that period. Using thermochemical energy storage compared to sensitive and latent heat storage gives the advantage of lossless heat storage over long periods of time without insulation.

Thermochemical heat storage (TCHS) can not only be used as a heat source in order to improve engine warmup but also for comfort applications, for example as auxiliary heating system.

1.2 Previous findings

This master thesis follows up on the findings of a previous research project called “Wärmespeicherung II”, carried out at the Technical University of Vienna, Austria and funded by the Research Association for Combustion Engines (FVV) eV.

During the project “Wärmespeicherung II” TCHS materials were examined for their suitability to be used in a TCHS system for motor vehicles. The TCHS materials were at first examined without a carrier material, therefore no TCHS composite was created. In a second step, $CaCl_2$ was chosen from the previously examined materials, to combine it with different carrier materials (e.g. glass wool, metal foam, silica gel, etc.) to form a TCHS composite. This composites were investigated for their applicability in a TCHS system. Glass wool proved to be the best option to form an effective TCHS composite.

Further a TCHS-system prototype was developed and tested in conjunction with a TCHS composite consisting of CaCl2 and glass wool.

Tests with this TCHS-system prototype showed a possible fuel consumption reduction during the NEDC by 1.35% but with a weight penalty of 22kg.

This led to the aspiration to reduce the weight penalty of a TCHS system for motor vehicles. Two approaches were stated during the “Wärmespeicherung II” project to overcome the weight and size problem of the TCHS system prototype: [4]

- The combination of previously unfeasible TCHS materials with a carrier material: TCHS composites could help to overcome the limitations some pure TCHS materials have (e.g. volume increase during sorption or insufficient sorbate transfer into the TCHS material). Enhanced TCHS composites could be key to reduce TCHS-system size and weight. [4]

- The concept of a TCHS system consisting of several small TCHS modules (respectively cartridges), placed directly at feasible locations of a motor vehicle (e.g. oil pan or coolant expansion reservoir). A system to transport engine coolant or oil to and from the TCHS is therefore no longer required, which can lead to a decrease in overall TCHS-system weight. Advantages in terms of system dynamics, due to the heat being released closer to the area where it is required and reduced cost due to common parts are anticipated. [4]

1.3 Goals and aims

Based on the findings and suggestions of the previous project, described in chapter 1.2, the goals and aims for this master thesis, which is part of the successor project called “Wärmespeicherung III”, were set.

Aim of this master thesis is to optimize an existing thermochemical heat-storage prototype in terms of specific storage capacity and reduced complexity. At first, different reversible thermochemical reactions should be examined to assess the feasibility of TCHS materials to be used under the working conditions, a motor vehicle poses for TCHS applications.

Further a simpler reactor design, than the existing prototype should be developed, while simultaneously optimizing charge and discharge characteristics.

Research on TCHS material should be focused on composite materials. Composite materials can be different mixtures of TCHS materials or a combination of TCHS materials and chemically inert materials, in order to gain a composite material with better properties, than base TCHS materials would have individually. [4]

The research reactor for TCHS composites is supposed to demonstrate the feasibility of a cartridge-style TCHS-reactor-concept, where small TCHS devices are placed directly where waste heat can be harvested and reused, instead of a big central TCHS device with heat exchangers for the distribution of heat.

1.4 Motor vehicle thermal management

Chapter 1.4 gives an overview of the fuel conversion characteristics for Otto- and Diesel-cycle engines.

Figure 1 shows the exergy flow of a Diesel-cycle engine. The base value for the different exergy flows is given by the exergy flow of the injected fuel (100%). It can be seen that only around 38% of the fuels exergy is used to overcome driving forces (air drag and rolling resistance). In this case, 15% of the fuels exergy is released as heat into the engine coolant, which can be used to charge a TCHS system.

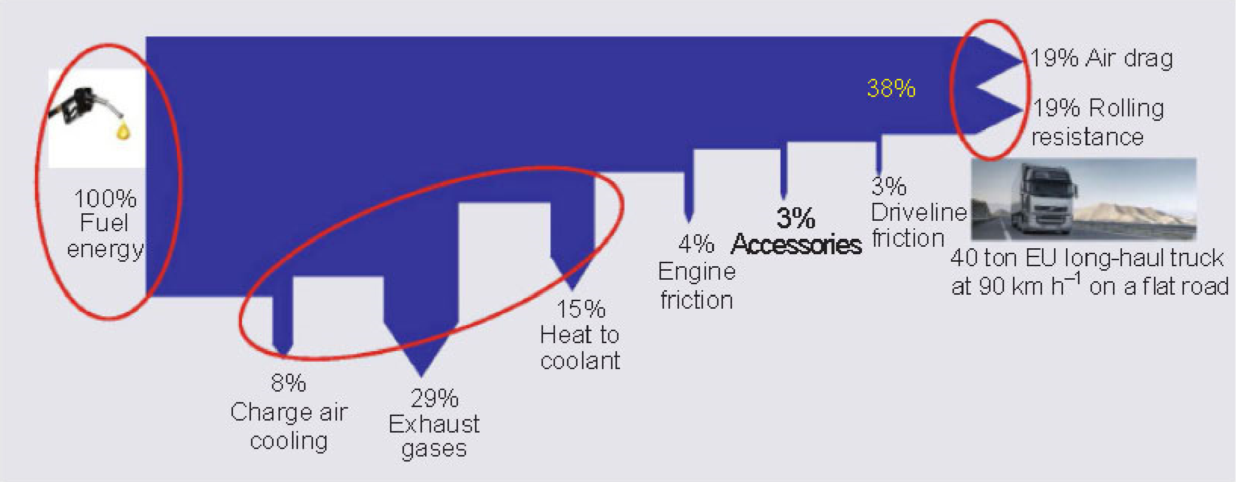

Figure 1: fuel conversion efficiency for a heavy duty diesel engine [5]

Figure 2 presents a fuel conversion efficiency outlook for a gasoline engine for passenger cars, from 2010 (present) to 2015 (future).

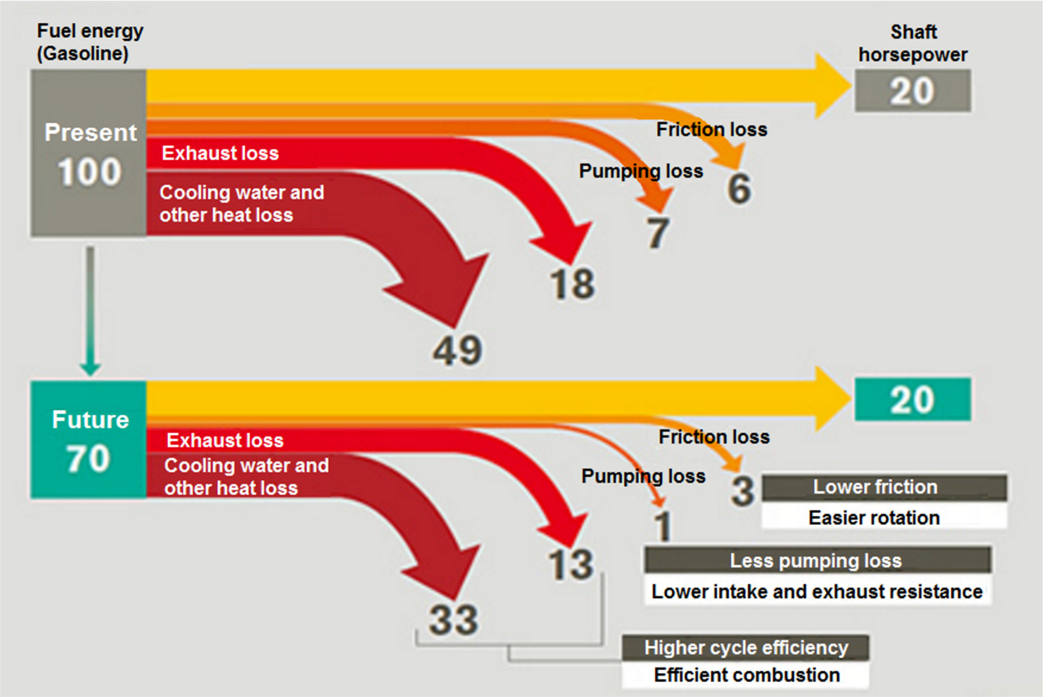

Figure 2: fuel conversion efficiency outlook (2010 to 2015) for gasoline engines by the NISSAN Motor Corporation [6]

Figure 1 and Figure 2 should provide an overview of the possible heat flows that can be used by an TCHS system that is fed by e.g. hot engine coolant.

Figure 3 shows the increase of fuel consumption during cold start and warmup phase of an engine. At the start of emissions tests (e.g. NEDC), in accordance with guideline 70/220/EWG by the Council of the European Union, vehicles have to be tempered to a temperature between 20-30°C. This leads to an increased momentary-consumption between 10-20%, relative to an engine at optimal working temperature. [7], [8]

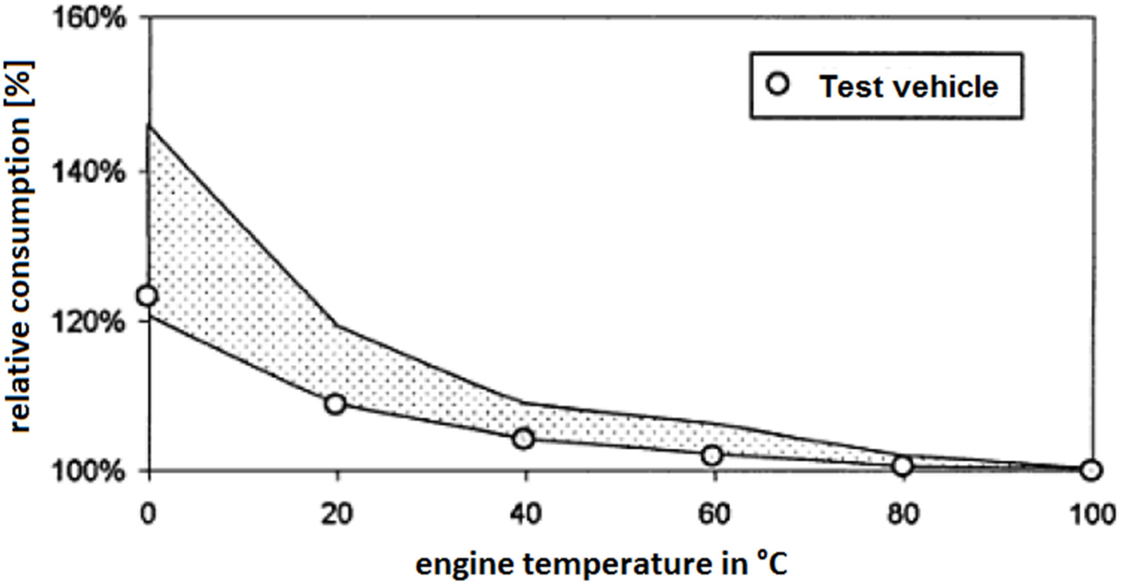

Figure 3: fuel consumption over engine temperature [8]
(translated from German)

This leads to the desire to shorten the warmup phase in order to minimize the efficiency penalty caused by suboptimal working conditions, which include increased friction as well as suboptimal combustion conditions due to increased heat loss through cylinder walls and fuel condensation effects. [8]

Measures in order to accelerate engine warmup include:

- Reduction of coolant flow
- PTC heating elements implemented into the cooling system
- Heat exchanger to transfer heat form exhaust gases to the engine coolant
- Enthalpy storage (sensible and latent)
- TCHS (thermochemical heat storage, prototype stage) [9]

A simulation of an idealised TCHS system (highest theoretically achievable heat release) implemented into a passenger car showed a possible fuel saving of up to 2% for a NEDC test and over 7% for a starting temperature of -7°C. The simulation showed potential for significant comfort gains in terms of a decreased cabin heat-up time of over 20% for tests at -7°C. This comfort gains could otherwise only be achieved by electrical heating systems which cause a significant increase in fuel consumption. [9]

1.5 Modular TCHS concept

Figure 4 (a) shows a TCHS concept where excess heat from the engine is transported via coolant fluid, through a heat transport system, into a TCHS system. In Figure 4 (a) engine coolant functions as a heat transfer fluid between the engine and the TCHS system. If the engine's oil is intended to be used as heat source/sink besides the engine's coolant, a heat exchanger has to be used to transfer heat between oil and coolant. Figure 4 (b) shows a modular TCHS system, where feasible locations are outfitted with independent TCHS modules.

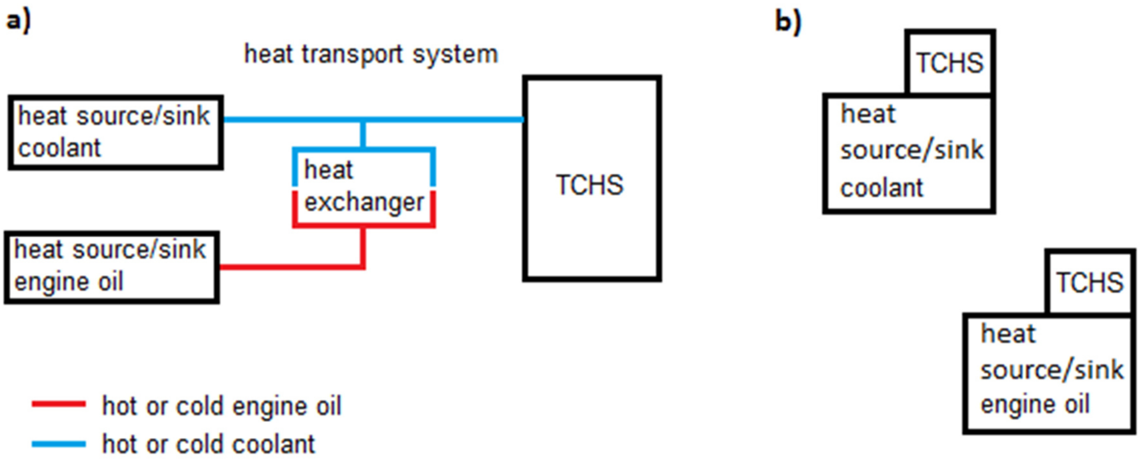

Figure 4: TCHS system connected to different heat sources via a heat transport system (a), modular TCHS system (independent TCHS modules providing heat storage capability on site) (b)

To utilise different media as heat sources for a TCHS system, heat exchangers are needed to transfer heat between the different media (e.g. engine coolant and oil). This makes for a complex heat transport system and heat loss during heat transport from/to the source/sink has to be considered and kept to a minimum.

Modular systems use one TCHS module per heat-source/sink location, therefore no heat transport system (including heat exchangers) is needed and no heat can be lost during transportation. Every TCHS system can be designed specifically for the location/medium it has to operate in/with. Due to the use of TCHS technology, no heat loss occurs during storage, therefore multiple smaller storage devices can be used, instead of one big storage device. One big storage device would be favourable with latent or sensible heat storage, because of its preferred surface to volume ratio, in order to keep heat loss small compared to the amount of stored heat.

The TCHS system, used for the experiments during this master thesis, is designed to represent the characteristics of a TCHS cartridge (module), utilised in a future modular TCHS-system. Figure 5 gives an overview of the cartridge-style TCHS concept for modular TCHS, intended for application in motor vehicles.

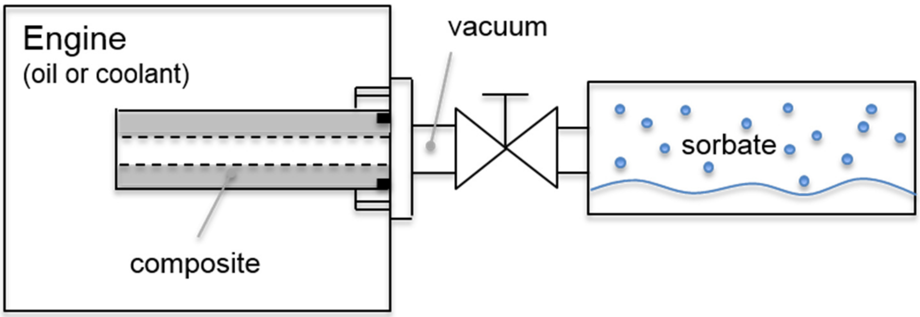

Figure 5: cartridge design concept of a TCHS system [10]

The heat exchange between the heat source (e.g. engine coolant) and the TCHS material works directly through the cartridge wall and does not require additional heat exchangers and heat transfer fluids. The connection between the TCHS material cartridge and the sorbate tank can be closed via a valve in order to store the heat. The entire system is evacuated until the gaseous phase in the system consists only of gaseous sorbate. During charging of the TCHS system, the hot medium around the cartridge (e.g. coolant) provides heat for the desorption of the TCHS material. The gaseous sorbate can condensate in the cooler sorbate tank. After desorption is completed, the valve is closed. To release stored heat, the valve is opened and the TCHS material absorbs sorbate. The released heat can be directly exchanged through the cartridge walls with the surrounding medium.

Advantages of a modular TCHS system are the lack of a heat transport system, less packaging constraints due to compact independent TCHS modules and a better adaptation for each TCHS module to the working conditions at the deployed location (e.g. engine coolant or oil). The lack of a heat transport system reduces complexity, weight and space requirements for the TCHS system.

2 Fundamentals of heat storage

2.1 Classification of heat reservoirs

Heat storage devices can be structured by different aspects:

- Temperature level: low, medium and high temperature applications
- Storage duration: short or long term storage
- Physical principle: sensible, latent and thermochemical
- Storage medium: e.g. water, salt, stone [11]

In this work a low temperature, long term, thermochemical heat storage system is used to research the feasibility of salts as TCHS materials.

2.2 Physical principles of heat storage

Figure 6 gives an overview of thermal energy storage structured by storage principles. The TCHS materials studied in this work (salt hydrates) belong to the category of sorption processes.

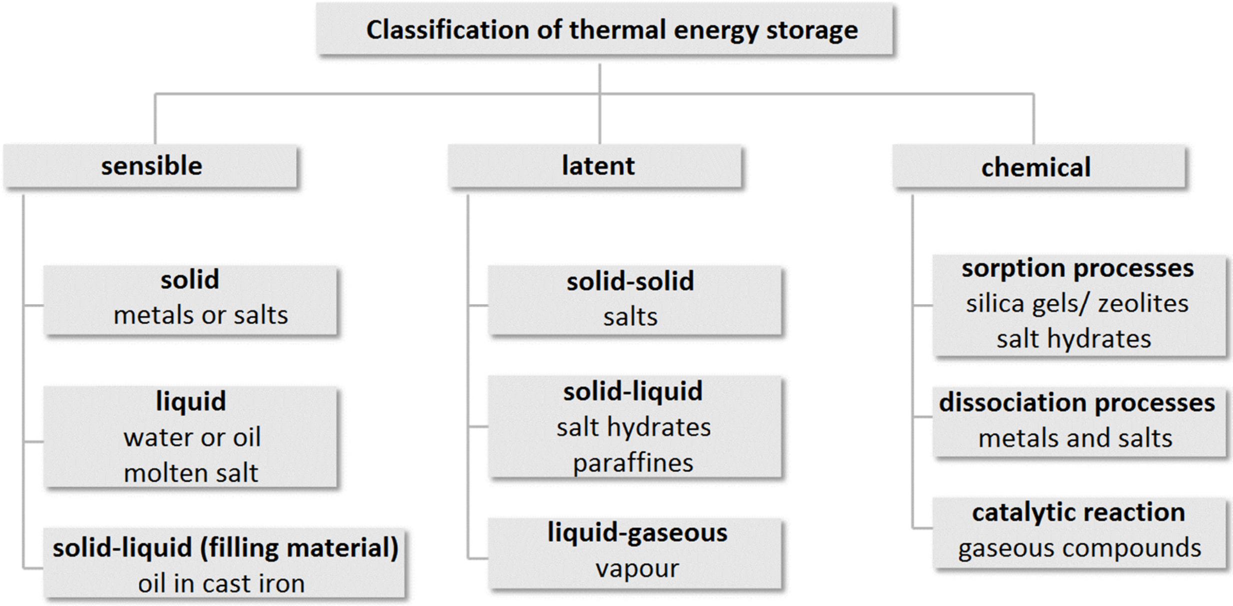

Figure 6: classification of thermal energy storage principles [4]
(translated from German)

2.2.1 Sensible heat storage

Sensible heat storage works by changing the temperature of a storage material (e.g. water). Therefore, temperature of a heat storage material increases during charging and decreases during discharging.

Equation (1) shows the correlation between the determining properties of a sensible heat storage and its heat storage capacity. [11]

$$Q = m_{storage} * c_{p-storage} * (\vartheta_2 - \vartheta_1) \tag{1}$$

Equation (1): heat storage capacity of a sensible heat storage reservoir [11]

$m_{storage}$	heat-storage-material mass
$c_{p-storage}$	heat storage capacity of the storage material
$\vartheta_2 - \vartheta_1$	temperature difference before and after charging
Q	heat stored during charging

To increase the storage capacity of a sensible heat storage, the mass of the heat storage material can be increased, a different material with higher heat storage capacity can be used or a higher temperature difference between fully charged and fully discharged can be utilised.

Main disadvantage of this storage principle proves to be a changing temperature level inside the storage during charging and discharging, due to the storage principle. For example, a fully charged sensible heat storage reservoir provides heat at a higher temperature level than an almost fully discharged reservoir. Further, great measures have to be taken (e.g. vacuum insulation) in order to minimize heat loss during storage.

2.2.2 Latent heat storage

Latent heat storage uses the phase change enthalpy of a storage medium to store heat. In contrast to sensible heat storage, as pictured in Figure 7, where the temperature level changes during charging or discharging, the temperature level in latent heat storage reservoirs stays almost constant during charging respectively discharging. Depending on the storage material and phase change (solid-liquid, liquid-gaseous), the temperature level varies where heat can be stored. Equation (2) shows the relation between heat storage capacity and the heat storage material properties. [11]

The heat storage capacity of latent heat storage devices depends on the mass of the heat storage material and the phase change enthalpy of the storage material as well as small sensible heat storage areas above and below the temperature of the utilised phase change. Therefore, to change the storage capacity either the mass of the storage material has to be altered or another material, with a different phase change enthalpy, has to be used.

$$Q = m_{storage} * [\int_{\vartheta_1}^{\vartheta_m} c_{ps} * d\vartheta + \Delta \mathrm{h_m} + \int_{\vartheta_m}^{\vartheta_2} c_{pl} * d\vartheta] \tag{2}$$

Equation (2): heat storage capacity of latent heat storage reservoirs (solid to liquid phase change) [11]

$m_{storage}$	*heat-storage-material mass*
Δh_f	*phase change enthalpy of the storage material*
$\vartheta_{m\,/\,1\,/\,2}$	*melting-, initial-, final-temperature of the phase change material*
c_{pl} / c_{ps}	*heat-storage-capacity of the phase change material in liquid/solid stage*

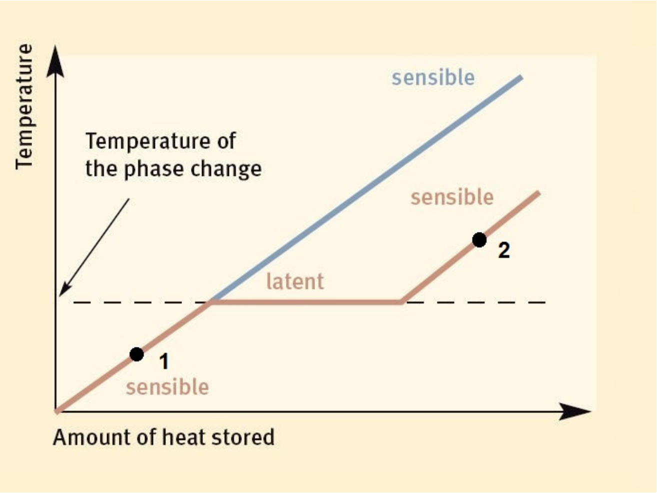

Figure 7: Temperature profile as a function of the amount of stored heat in the case of storage of sensible heat and latent heat, © ZAE Bayern [12]

2.2.3 Thermochemical heat storage

Figure 8 gives an overview of different working principles of chemical heat storage and examples for each principle.

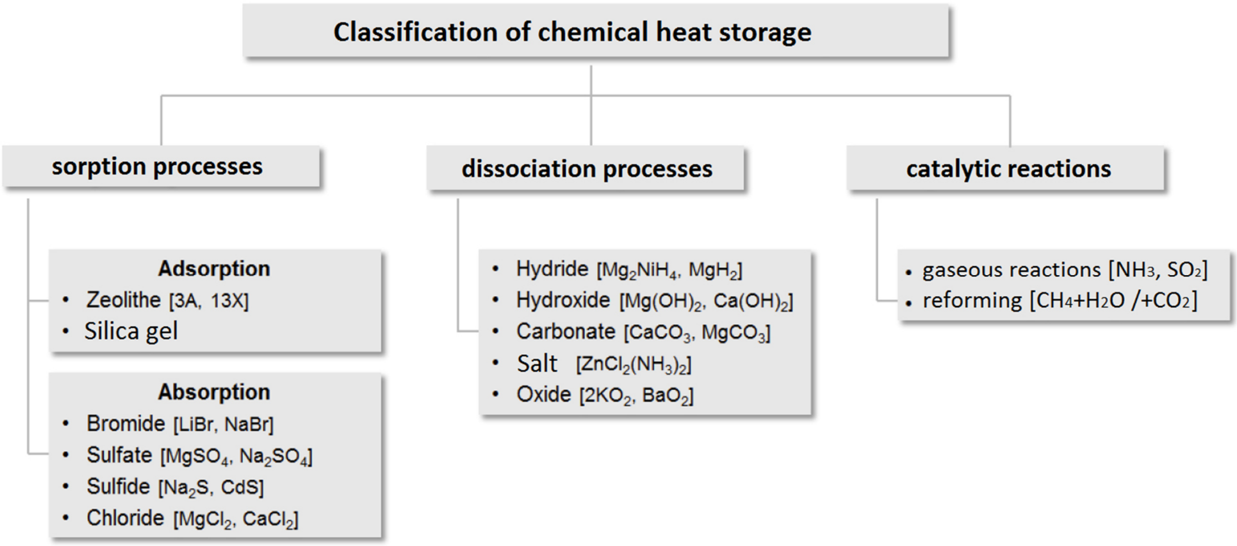

Figure 8: classification of chemical heat storage by working principle [13]
(translated from German)

Thermochemical heat storage uses reversible chemical reactions to store heat. Figure 9 shows the concept of TCHS. To charge heat storage material, heat has to be applied to the storage material in order to enable an endothermic reaction and separate the starting products of the exothermic reaction. During heat storage the reacting agents are stored separately. To discharge a TCHS, the reacting agents are combined in order to react exothermic and release stored heat.

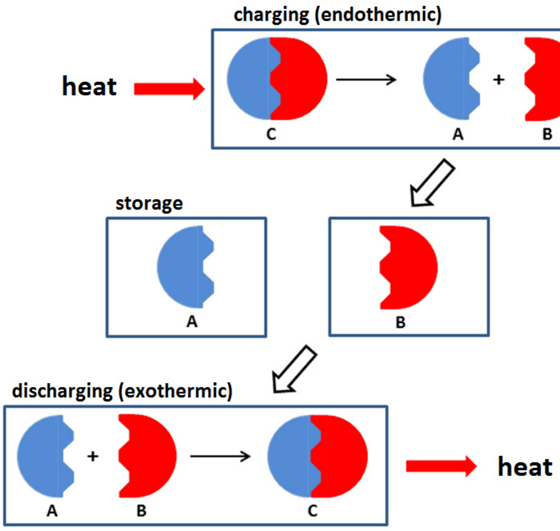

Figure 9: working principle of TCHS, © Fraunhofer UMSICHT [14]
(translated from German)

Thermochemical storage is determined by two different mechanisms, which control reversible reactions that greatly influence the characteristics of the reaction: [15]

- Physical adherence: low strength bonding forces like Van der Waals forces
- Chemical adherence: high strength bonding forces like covalent, metallic and ionic bonds

Physical sorption generally takes place at lower temperatures and decreases with temperature increase, whereas chemical sorption generally takes place at higher temperatures which act as activation energy for chemical bonds to form. [16]

The TCHS materials researched in this work use physical adherence to absorb sorbates.

2.3 Benefits and drawbacks of different heat storage principles

Sensible heat storage is the simplest principle of heat storage and is widely used in thermos flasks or domestic hot water tanks to provide hot water for e.g. sanitary applications. Drawbacks of sensible heat storage are changing temperature levels during operation and the requirement for insulation to minimise heat loss. Heat loss cannot be completely prevented and therefore storage times are limited in order to achieve a benefit. For some sensible heat storage materials, like molten salt, ambient temperatures are not high enough to prevent discharged storage material (molten salt) to further lose heat and remain molten. This leads to a need for process control that monitors storage material temperatures and allows to keep storage material in the preferred state (e.g. liquid for molten salt). This sometimes requires an alternative possibility (e.g. auxiliary heating device) to balance heat loss when a discharged storage cannot be charged as intended (e.g. by solar heat).

To be able to store heat without the drawbacks of a changing temperature level during operation, latent heat storage systems were invented. A constant temperature level during operation poses an advantage, as well as high heat storage capacity without need for a high temperature difference like sensible heat storage. Disadvantages of latent heat storage systems are the need for insulation and a fixed temperature level depending on the utilised storage material and phase change. Due to unavoidable heat loss, storage time in latent heat stores is similarly limited like in sensible heat stores.

Thermochemical heat storage eliminates the need for insulation to store heat. Storage time is therefore just limited by the chemical stability of the TCHS material and the ability to store both reaction components leak free. This enables longer storage times without heat loss and theoretically higher heat storage densities than sensible and latent heat storage systems as shown in Table 1, potentially enabling new heat storage applications. [17]

Table 1: heat storage densities for different storage principles [18]

Storage type	Maximum energy density
Sensible heat storage Principle: heat supply	50 - 60 kWh/m^3 for water (temperature difference 50 K)
Latent heat storage Principle: phase change	50 – 120 kWh/m^3
Thermochemical heat storage Principle: adsorption	200 – 250 kWh/m^3

Drawbacks respectively obstacles of TCHS systems are their relatively early development stages and therefore further research is necessary. [19]

2.4 Investigated TCHS materials

The chosen TCHS materials to investigate, were focused on high possible energy density and low storage temperature in order to be feasible candidates for an application in motor vehicles, where maximum fluid temperatures (e.g. engine oil or coolant) for storage purposes had to be taken into account. Figure 10 gives an overview of the field of possible storage materials. The materials chosen for experiments were $MgCl_2$, $MgSO_4$, $CaCl_2$, $Al_2(SO_4)_3$ and LiBr, which tend to have favourable properties for the intended application. Further properties like toxicity and safety issues as well as price and availability of TCHS materials are characteristics to be regarded in the following chapters (2.4.1 to 2.4.5 and 5).

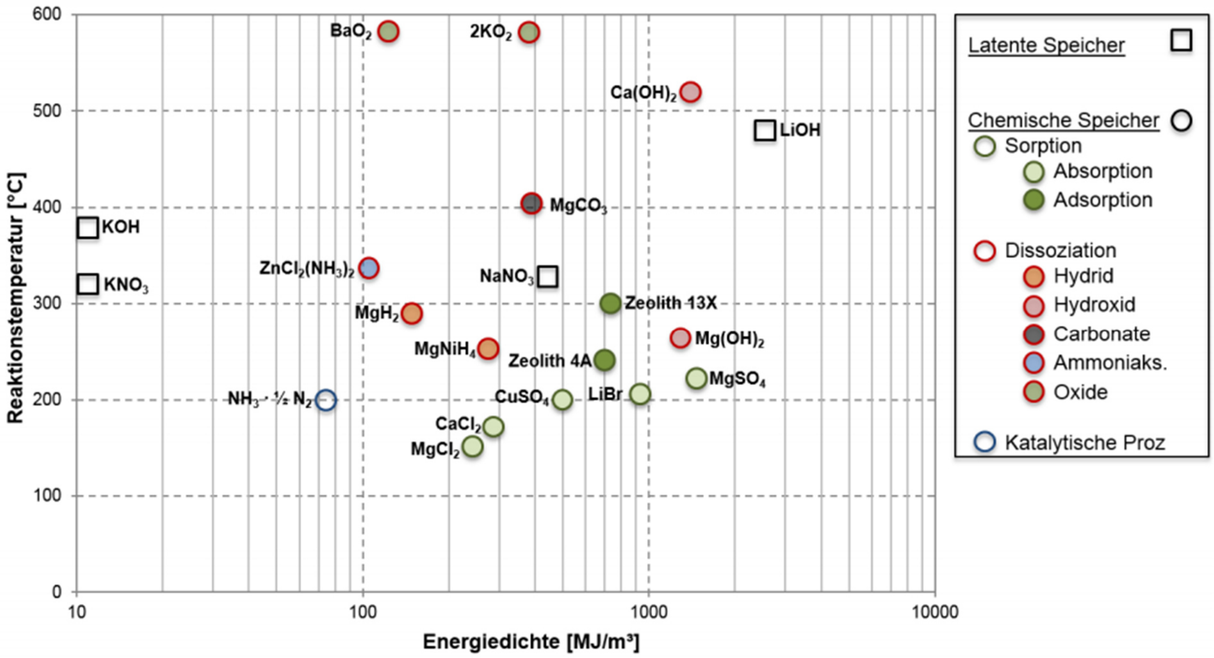

Figure 10: Energy densities of various storage processes and -materials [4]

2.4.1 Calcium chloride - $CaCl_2$

$CaCl_2$ is a white, odourless, extremely water soluble salt that forms hydrates under heat release. Equation (3) shows the reaction equation of $CaCl_2$ hydration. [20]

$$CaCl_2 + 6H_2O \leftrightarrow CaCl_2 * 6H_2O + 361{,}2\ kJ/mol_{CaCl_2} \tag{3}$$

Equation (3): reaction equation of $CaCl_2$ hydration (hexahydrate) [21]

Figure 11 shows the hydration curve of $CaCl_2$. The hydration curve indicates that complete dehydration of $CaCl_2$ hydrate, with a dehydration temperature below 150°C, seems possible, therefore $CaCl_2$ poses a viable TCHS material candidate regarding waste heat and solar applications. [22], [23]

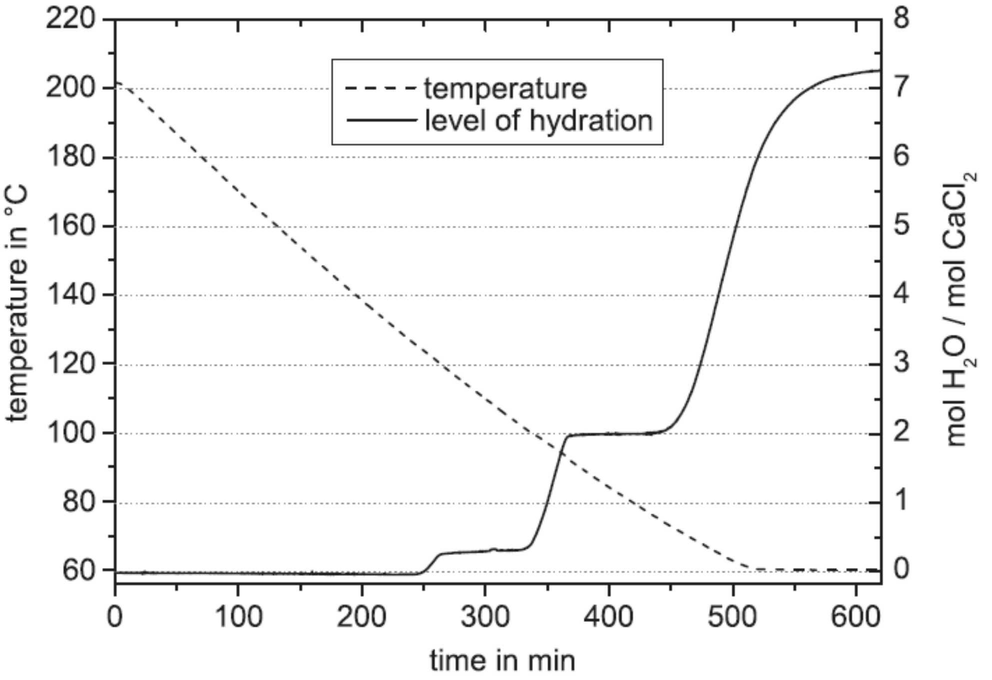

Figure 11: dynamic hydration of $CaCl_2$ at a partial pressure of 5 kPa and a cooling rate of -0.4K/min [22]

Figure 12 shows hydration (a) and dehydration (b) of $CaCl_2$ between the anhydrous and dihydrate state of $CaCl_2$ at different H_2O partial pressure levels. It becomes apparent that the H_2O partial pressure level has an influence on hydration/dehydration characteristics, but also if $CaCl_2$ hydrates or dehydrates via the same hydration steps, respectively the same temperatures for reaching a dedicated hydration step during hydration or dehydration. In general hydration takes place on lower temperature levels than the corresponding dehydration to reach the same hydrate level. A similar effect of heating/cooling rates affecting onset temperature for hydration/dehydration of storage materials has also been shown for $MgSO_4$. [17], [22]

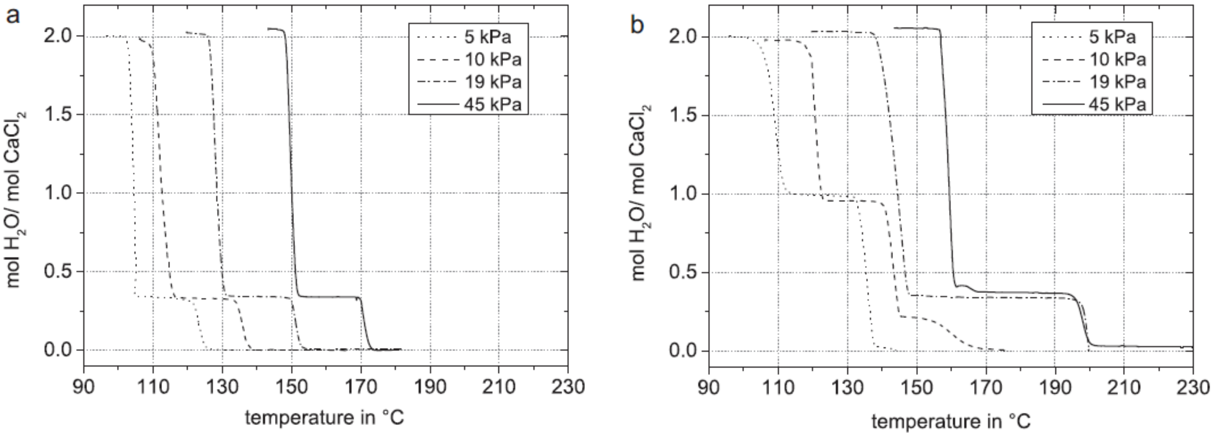

Figure 12: (a) Level of hydration during dynamic hydration of CaCl2 at different H2O partial pressures with a cooling rate of −0.2 K/min. (b) Level of hydration during dynamic dehydration of CaCl2·2H2O at different H2O partial pressures with a heating rate of 0.2 K/min. [22]

Depending on, if temperature treatment of a material is executed before a hydration/dehydration cycle or not, the material behaves different during dehydration. With previous temperature treatment (heating to 200°C) $CaCl_2$ does not fully reach the anhydrous state during dehydration at 131°C, instead $CaCl_2$*$0.3H_2O$ forms, without additional heat treatment the anhydrous state is achieved. It is assumed that this effect occurs due to increased crystal integrity of $CaCl_2$ or a changed particle size distribution. This metastable 0.3-hydrate state of $CaCl_2$ also appears depending on the water vapour pressure level during dehydration as shown in Figure 12. It seems to be preferable to avoid formation of the 0.3-hydrate state during dehydration in order to achieve full dehydration (fully charged TCHS material) with lower charging temperatures. [22]

Cycle stability for CaCl2 seems to be positive. Different research states, that for repeated 4-hydrate [24] / dihydrate [22] to anhydrous state desorption and sorption runs, no changes in sorption and desorption characteristics were observed.

Uses of $CaCl_2$ and aqueous $CaCl_2$ solutions include de-icing, dust control, heat transfer fluid and binding agent for concrete. [20]

$CaCl_2$ is classified as material that causes eye irritation according to regulation (EG) Nr. 1272/2008 and guideline 67/548/EWG or 1999/45/EG, which correspond to the risk and safety statements H319 and R36 mentioned in the safety data sheet of the material, concerning eye irritation. [25]

2.4.2 Magnesium sulphate - $MgSO_4$

Magnesium sulphate is a colourless, odourless, strongly hygroscopic solid with a bitter taste and good aqueous solubility. Magnesium sulphate is able to form hydrates in an exothermic reaction, as it is shown in Equation (4) for the formation of heptahydrate.

$$MgSO_4(s) + 7H_2O(g) \leftrightarrow MgSO_4 * 7H_2O(s) + 411kJ/mol_{MgSO_4} \tag{4}$$

Equation (4): reaction equation for the formation of magnesium sulphate heptahydrate [17]

Current fields of application of magnesium sulphate except TCHS, are fertilizer, chemical drying agent and several medical applications (e.g. cardiac applications). [26], [27]

Figure 13 shows the dehydration characteristic of $MgSO_4$ heptahydrate in terms of mass loss over temperature and a differential scanning calorimetry signal (DSC). The mass loss curve shows clearly, that most desorption takes place below 150°C and therefore in a very applicable temperature range for industrial applications, e.g. solar energy. [17]

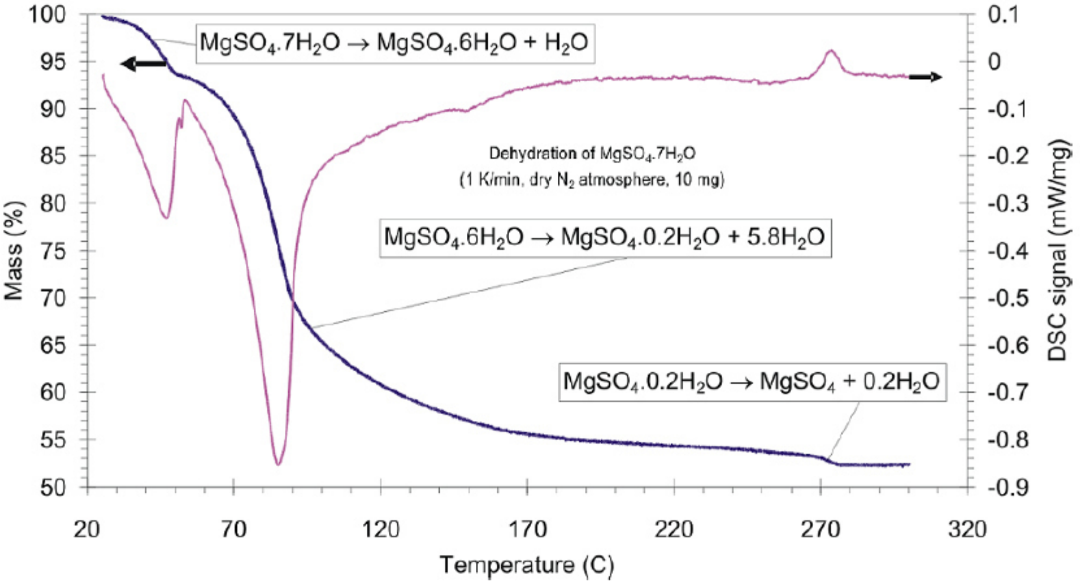

Figure 13: Dehydration of $MgSO_4*7H_2O$ [17]

Figure 14 shows the influence of different heating rates on the positions (temperature levels) where dehydration peaks respectively dehydration steps occur. Higher heating rates lead to higher desorption temperatures. [17]

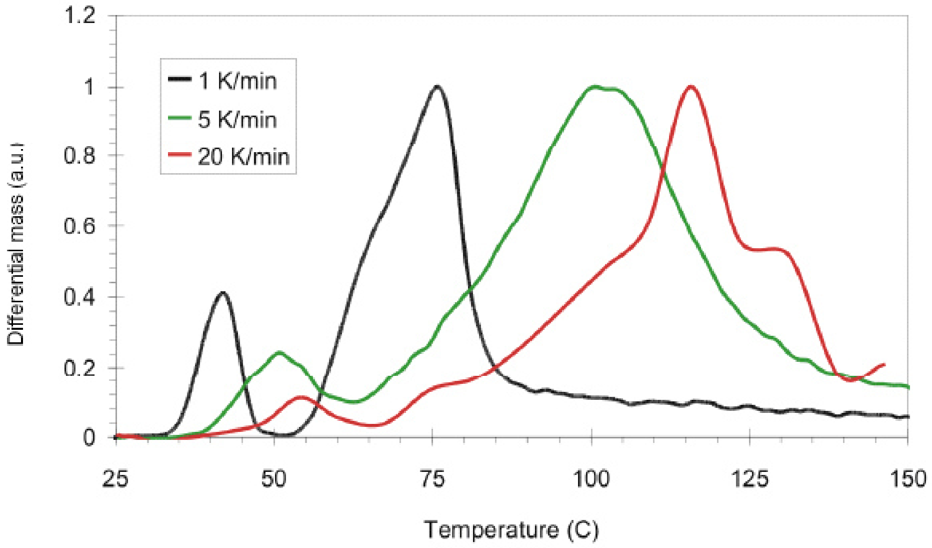

Figure 14: influence of heating rate on dehydration peaks of $MgSO_4$ [17]

During dehydration of $MgSO_4$ heptahydrate melting can occur in the temperature range of 48-52°C. This effect appears if dehydration speed is slow compared to heating rates, which happens to be at high heating rates and large samples respectively large $MgSO_4$ particles. Melting poses a problem because it reduces porosity of $MgSO_4$ beds as shown in Figure 15 and can therefore hinder water vapour transport through the material. [17]

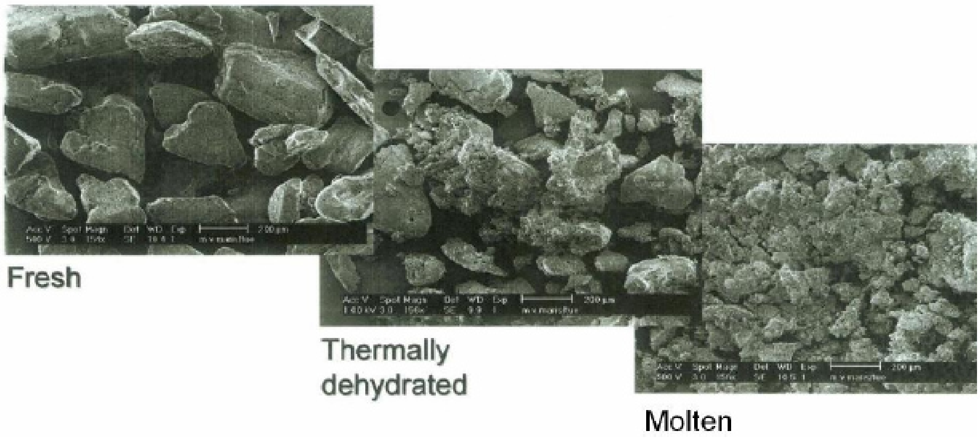

Figure 15: $MgSO_4$ particle structure [17]

A good hydration characteristic is important for application as TCHS material, cycle stability and complete dehydration as well as fast reaction kinetics at working conditions are preferable too.

$MgSO_4$ poses good dehydration characteristics and particle size shows little effect on hydration speed (Figure 16). Layer thickness has a considerable effect on hydration speed, which indicates vapour transfer through the material is a limiting factor for the hydration reaction. Cycle stability of the material is good, but slow hydration speeds and decreasing water-uptake/hydration speed during hydration under increased temperature levels pose a field for further research to improve these characteristics. [17]

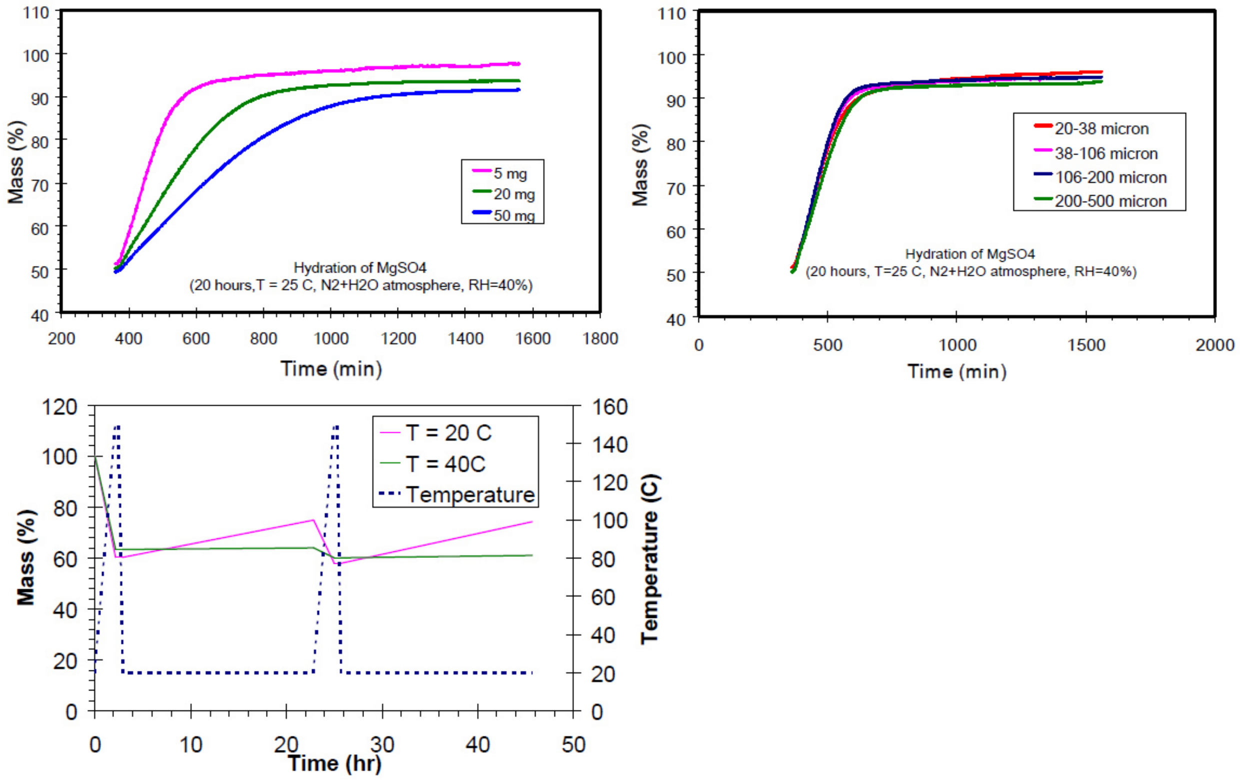

Figure 16: effect of layer thickness (top left, 20mg equals roughly 1.5 mm)
effect of particle size (top right)
cycle stability and effect of different temperature levels on hydration (bottom left) [17]

Magnesium sulphate hydrate ($MgSO_4 * xH_2O$) is considered to be a non-dangerous material, corresponding to regulation (EG) Nr. 1272/2008 and guideline 67/548/EWG or 1999/45/EG. Magnesium sulphate is non-flammable and no special environment protection measures have to be taken. [28]

2.4.3 Aluminium sulphate - $Al_2(SO_4)_3$

Aluminium sulphate is a white, water soluble, non-flammable, hygroscopic salt. $Al_2(SO_4)_3$ can form various hydrates including $Al_2(SO_4)_3 * 14\ H_2O$.

Usage of $Al_2(SO_4)_3$ includes flocculation agent for water purification as well as additive during paper production. [29] [30]

Equation (5) gives the dehydration reaction of aluminium sulphate.

$$Al_2(SO_4)_3 * 14H_2O \leftrightarrow Al_2(SO_4)_3 * 0.4H_2O + 615.9kJ/mol_{Al_2(SO_4)_3} \qquad (5)$$

Equation (5): dehydration reaction of $Al_2(SO_4)_3$ hydrate [29]

Figure 17 shows results of a TGA and a DSC analysis of aluminium sulphate hydrate. Two dehydration cycles with DSC and TGA analyses were executed. At first 14-hydrate was dehydrated up to 355°C (Figure 17), then dehydrated up to 155°C (Figure 18). Both cycles reached the 0.4-hydrate state. Comparison of those two dehydration cycles shows that the 0.4-hydrate state can be reached with 155°C dehydration temperature, but heating rate and maximum heating temperature influence dehydration speed. An increase in heating rate and increased maximum temperature lead to increased dehydration speed. [29]

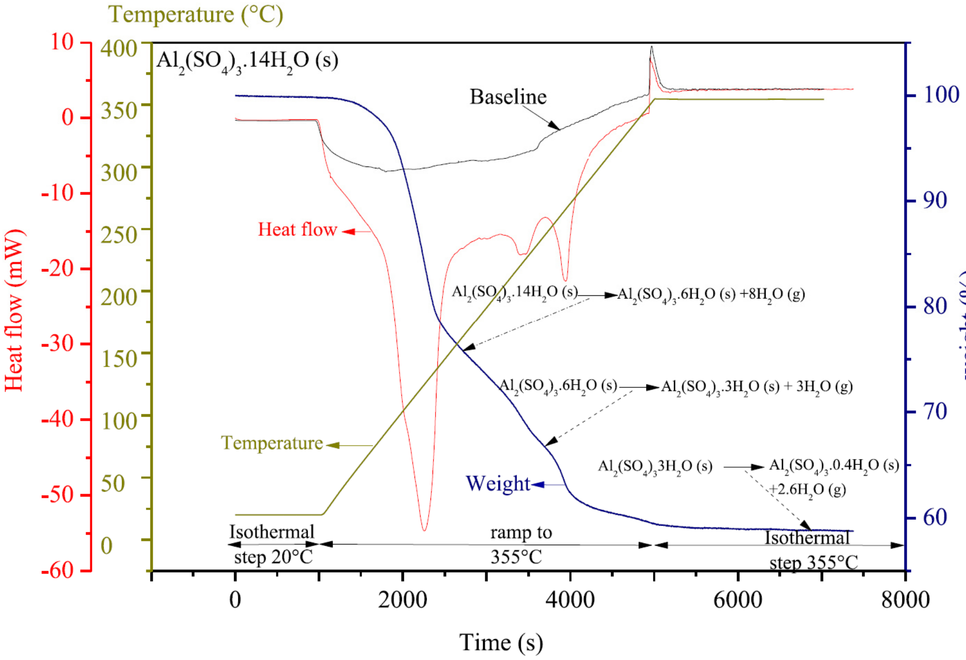

Figure 17: TGA and DSC (heating rate: 5°C/min) analysis of aluminium sulphate hydrate dehydration [29]

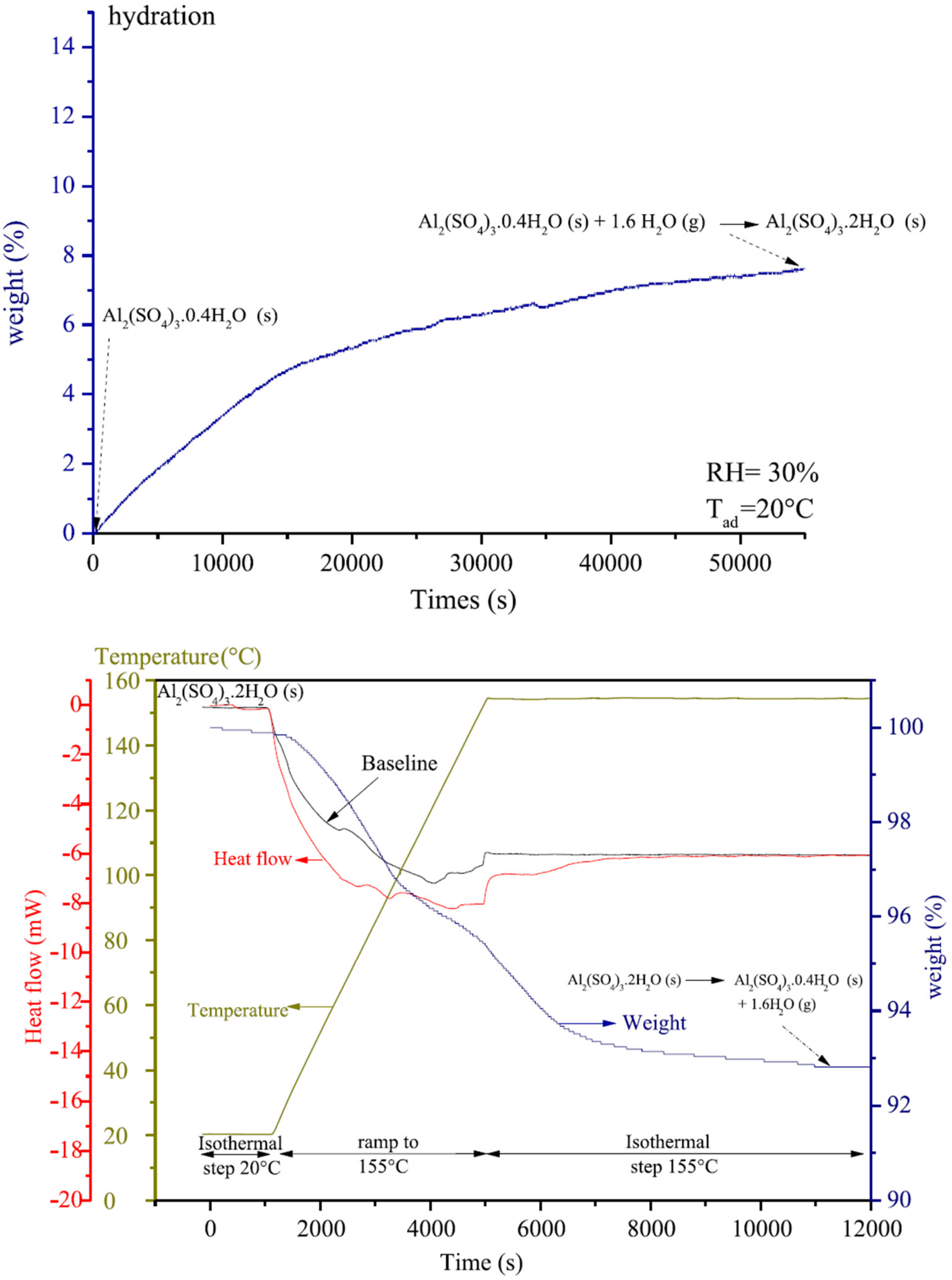

Figure 18: hydration (top) and dehydration (bottom) of $Al_2(SO_4)_3$ (heating rate: 2°C/min) [29]

Hydration of $Al_2(SO_4)_3$ under relative humidity of 30% and T = 20°C (equivalent to a H_2O vapour pressure of 7 mbar) for more than 13h leads to a water uptake of only 1.6 mole per mole $Al_2(SO_4)_3$, therefore releasing approximately only 20% of the heat which was stored during dehydration. A carrier material with high specific surface is suggested to improve hydration speed. [29]

Regarding regulation (EG) Nr. 1272/2008, aluminium sulphate is corrosive to metals (category 1, H290) and can cause severe eye damage (category 1, H318). [30]

2.4.4 Lithium bromide – LiBr

Lithium bromide is a bitter tasting, colourless, highly hygroscopic salt. Waterless LiBr will absorb water out of humid air until an aqueous solution forms.

Lithium bromide is used in air conditioning applications, working by the absorption principle, in form of a 50-60% aqueous solution. Further applications are chemical reactions like dehydration of organic compounds or as part of catalysts as well as in experimental batteries and as drugs like sedatives and hypnotics. [31] [32]

Table 2 and Figure 19 show the possible hydration steps for LiBr under atmospheric pressure and lower than atmospheric pressure.

Table 2: hydration steps for LiBr at atmospheric pressure [33]

Hydration number of LiBr	Decomposition temperature of the hydrate [K]
5	223
3	280
2	315

It can be seen that LiBr cannot absorb as much water per part LiBr than other materials examined, especially when the low decomposition temperatures of higher LiBr-hydrates are taken into account. It can be seen that for temperature levels slightly higher than 0°C the 3-hydrate state of LiBr becomes unstable, therefore for ambient temperatures around 20°C only the 2-hydrate state for LiBr can be achieved.

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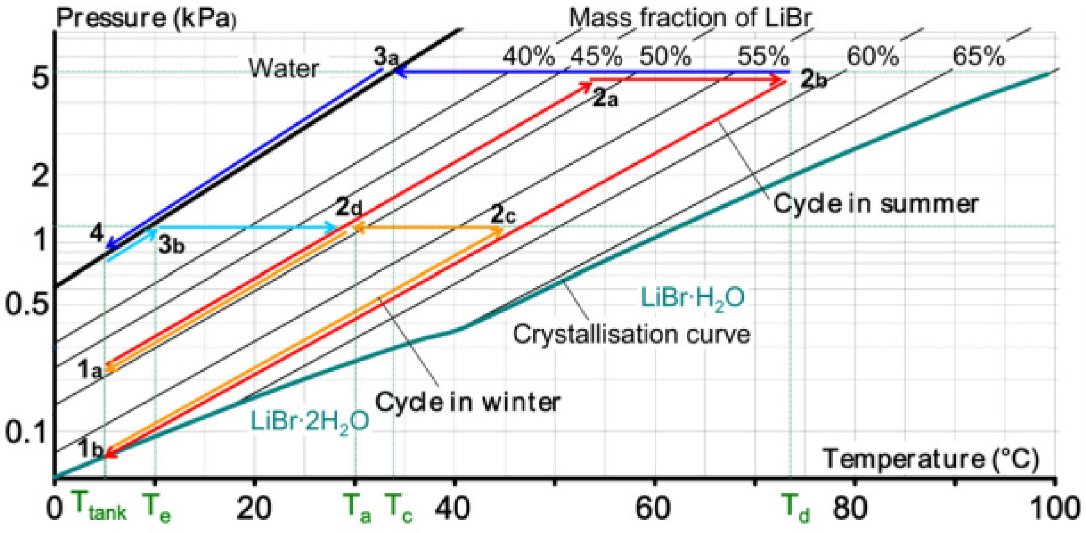

Fig. 3. Dühring chart of lithium bromide/water cycle in annual absorption heat storage process.

Figure 19: Dühring-chart of a lithium bromide/water cycle for an annual heat storage cycle [34]

Figure 19 presents possible mixing ratios for LiBr and water dependent on the boundary conditions pressure and temperature, as well as absorption cycles for winter and summer operation of a heat storage process.
The most interesting curve of Figure 19, regarding the intended application of LiBr in this work, poses the crystallisation curve of LiBr. The crystallisation curve poses the boundary for LiBr to not liquefy under presence of water.

According to regulation (EG) Nr. 1272/2008, LiBr is considered to be acute orally toxic (category 4, H302) and cause skin irritation (category 2, H315), eye irritation (category 2, H319) and may cause an allergic skin reaction (category 1, H317). LiBr is non-flammable but dangerous gases can develop due to an external fire. [35] [36]

2.4.5 Magnesium chloride - $MgCl_2$

Magnesium chloride forms colourless, bitter tasting, hexagonal crystals that have a high water solubility. $MgCl_2$ has the ability to form hydrates in an exothermic reaction given by Equation (6) for $MgCl_2$ hexahydrate. Figure 20 shows the desorption characteristic of $MgCl_2$. Complete dehydration occurs around 200°C but almost 80% of the enthalpy change between $MgCl_2$ and $MgCl_2$*$6H_2O$ occurs between $MgCl_2$*$1H_2O$ and $MgCl_2$*$6H_2O$. Therefore, lower desorption temperatures below 150°C, which are easier achievable e.g. with solar heat or waste heat, are applicable to utilise that potential. [37]

$$MgCl_2 + 6H_2O \leftrightarrow MgCl_2 * 6H_2O + 406{,}8kJ/mol_{MgCl_2} \tag{6}$$

Equation (6): reaction equation for the formation of magnesium chloride hexahydrate [38]

$MgCl_2$ shows a highly hygroscopic characteristic, to the point that dry $MgCl_2$ in humid air fluidises to form an aqueous solution. Cases of "over-hydration" were found, where $MgCl_2$ absorbed so much water that it started to fluidise and form a gel like structure. For dehydration of $MgCl_2$ above 135°C, it was found that HCl was formed. This leads to $MgCl_2$ breakup and therefore degeneration of the storage material and HCl is highly corrosive. [39]

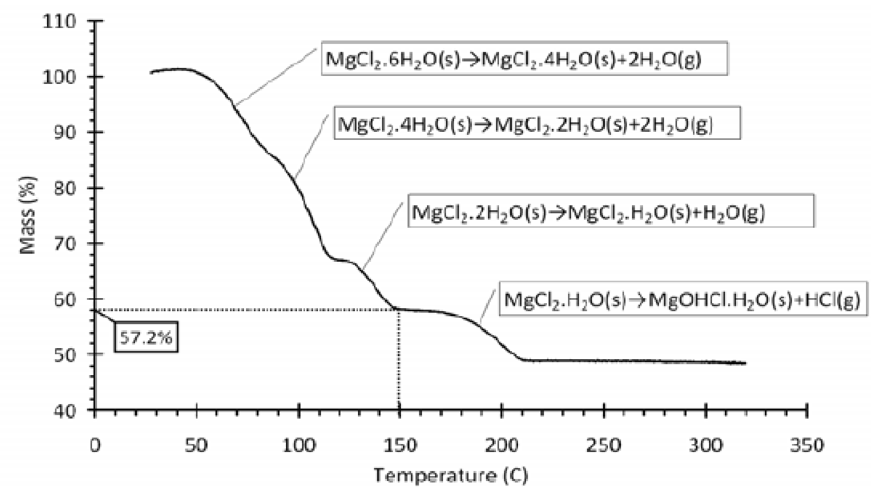

Figure 20: TGA measurement of $MgCl_2*6H_2O$ (heating rate 1°C/min in dry nitrogen atmosphere, sample mass 10 mg) [39]

It is suggested to keep dehydration temperatures below 135°C to prevent HCl formation and use a carrier material to form a composite, in order to stop $MgCl_2$ to overhydrate and therefore hinder gas transfer through the storage material. Figure 21 shows the created composite (top left) and the pressure drop (bottom) when humid air is pushed through an open sorption reactor (top right), using pure $MgCl_2$ (pink) or a composite (blue) as TCHS material. [39]

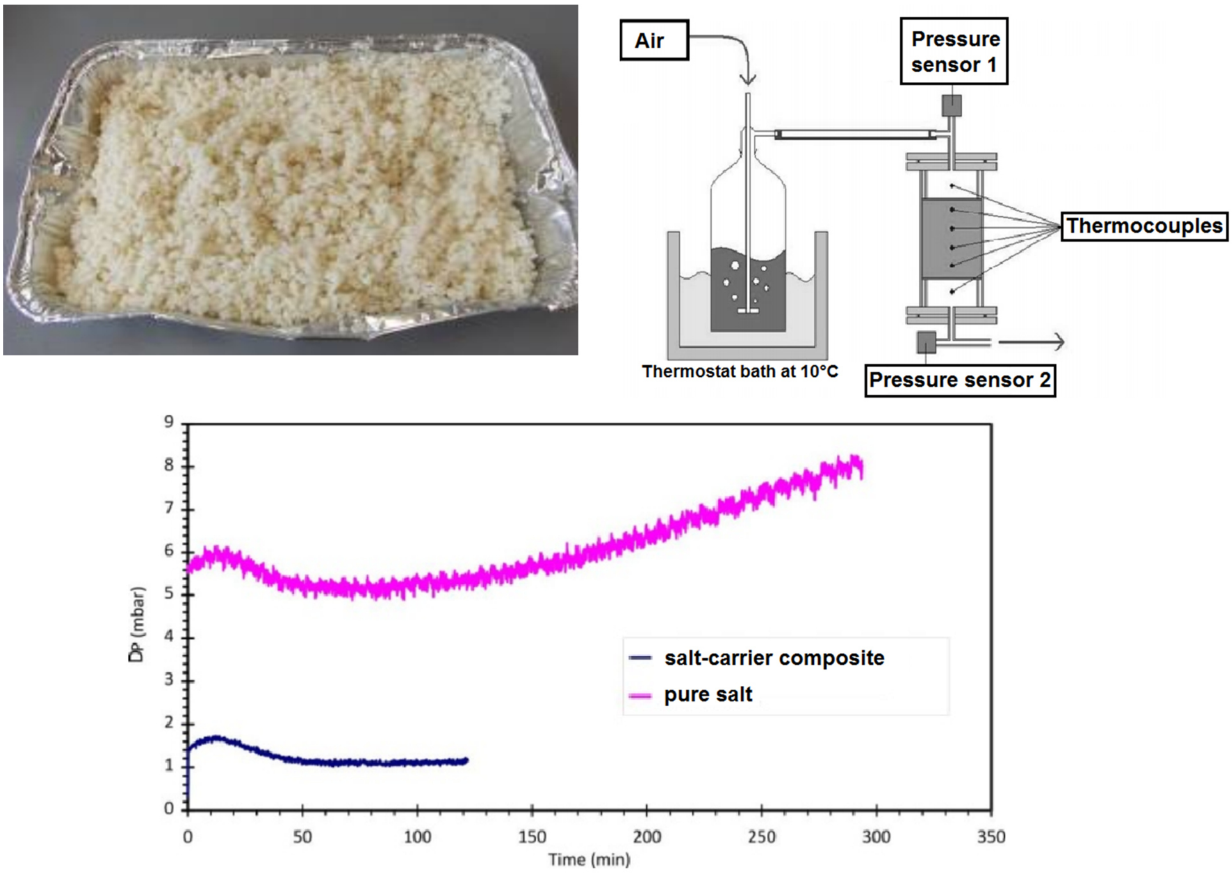

Figure 21: Composite of $MgCl_2$ hydrate with carrier (left), pressure drop over reactor using composite material, compared to using pure salt [39]

Anhydrous $MgCl_2$ is mainly used for electrolytic production of magnesium metal. Further $MgCl_2$ has a wide range of applications in other industries for example as part of binding agents (Sorel cement), feed additive for livestock (magnesium source), de-icing agent and TCHS material. [40]

$MgCl_2$ and $MgCl_2$ hexahydrate is considered to be a non-dangerous material, corresponding to regulation (EG) Nr. 1272/2008 and guideline 67/548/EWG. The Materials are non-flammable and no special environment protection measures have to be taken. [41] [42]

2.5 Composite materials for TCHS

Composite TCHS materials are composed of two or more materials of which at least one has to be a TCHS material. Composite materials use properties of their base materials to create a new set of properties with the objective of creating a better TCHS material.

Composites can be categorized as follows:

- Mixture of two or more TCHS materials, e.g. LiCl + LiBr [43]
- Chemically inert carrier material impregnated or coated with TCHS material, e.g. impregnated glass wool [13]
- active TCHS carrier material impregnated or coated with TCHS material, e.g. Zeolites impregnated with TCHS material [29]
- Porous or non-porous carrier materials [13]

Following advantages for the use of carrier materials are stated [13] :

- Increased sorbate uptake due to improved diffusion characteristics
- Improved material stability during cycling loads
- Reduction of volume change during operation
- Fixation of TCHS material by the carrier material, therefore hindering leakage of TCHS material
- possible Improvement of thermal conductivity

Crucial criteria for the selection of a suitable carrier material is the chemical stability of the carrier regarding the TCHS material (absorber) and the utilised sorbate (e.g. water or methanol). A chemical reaction between the TCHS material and the carrier would continuously destroy the TCHS material and therefore reduce storage capability. Stability of the carrier material has to be ensured in the temperature and pressure ranges it is exposed to during operation. Carrier material surface characteristic influences not only properties like vapour transport capability through the composite and impregnation characteristic of the carrier material with TCHS material but also deliquesce characteristics of TCHS materials (salts). Thermal conductivity and density of carrier materials pose important properties. [13] [44]

Carrier materials for TCHS applications can be either impregnated or coated with TCHS material. Impregnation needs the carrier material to be open-porous, where a solution (e.g. aqueous) of the TCHS material can be soaked up by the carrier material and after drying TCHS material deposits are formed inside the pores. Materials with this characteristic are e.g. porous glass filter or expanded graphite. [13] [45]

In contrast, on non-porous materials like glass fibres, TCHS material deposits can only be formed on the surface of the carrier material (adsorption). [13]

2.6 Constraints of TCHS in motor vehicles

Motor vehicles present a special environment for TCHS applications because of specific constraints. Those constraints are caused by the fact that motor vehicles are limited in size and weight, especially when seen in contrast to stationary applications. Devices for mobile applications are far more prone to experience harsh working conditions like vibrations and changing temperature levels. For example, a TCHS device for building heating located in a basement does not experience high temperature changes and vibrations/impacts, a TCHS device intended for the use in motor vehicles would experience. Further, the aspect that motor vehicles possess a high risk of being subject of an accident leads to the necessity of elevated safety standards compared to stationary applications of TCHS, in order to prevent major additional safety hazards (e.g. flammability or toxicity) by the TCHS device during an accident.

Another specific characteristic for TCHS in vehicles, poses the focus on power density rather than energy density. TCHS applications are intended to provide additional heat during cold start and warmup phases to supplement the vehicles waste heat flow used to generate optimal working temperatures. Therefore, the TCHS system has to be able to provide a significant amount of heat in a short period of time, with a reaction time (time from activation to peak power) as short as possible, in order to contribute to a reduced vehicle warmup time.

2.7 Impact of heat transfer area size on TCHS reactor performance

Heat-transfer-area size poses an important factor to achieve a high heat-release power-output. Reactors utilized in prior research projects, used copper fins soldered to a copper tube in order to increase their heat exchange area. Figure 22 and Figure 23 give an impression of the importance of an increased heat exchange area. Both figures show data of heat release experiments with maximum heat release power for both figures in the range of 300 ± 25W but with a significant difference in TCHS material mass. [13]

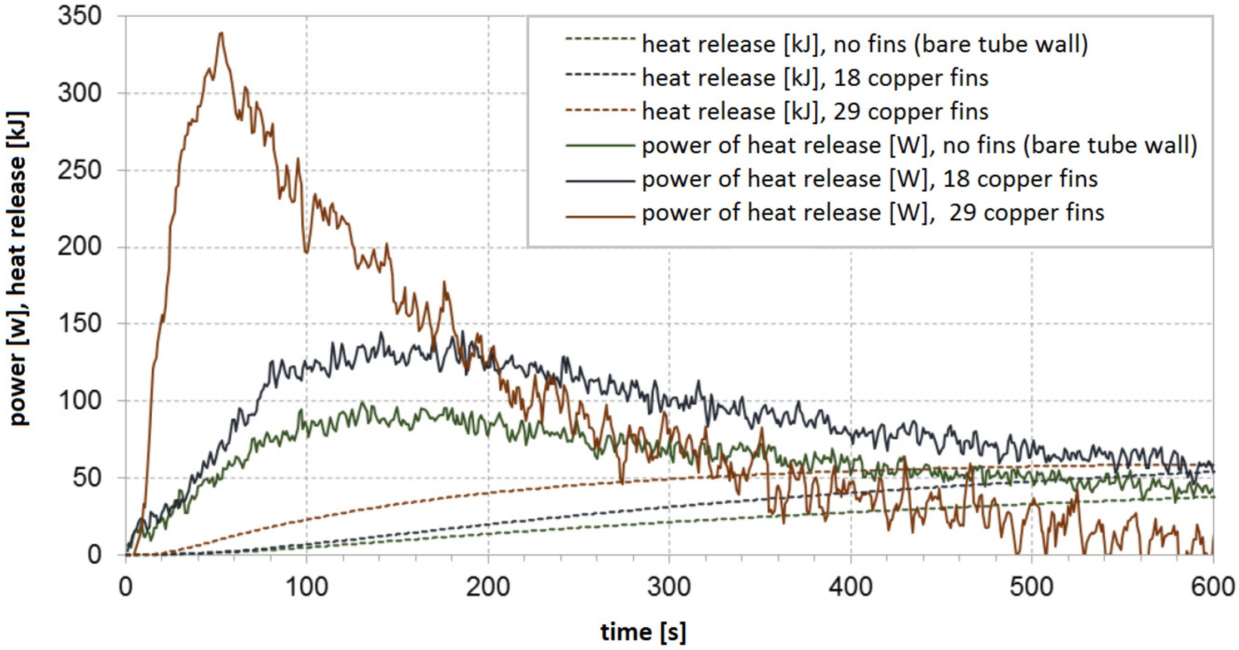

Figure 22: increase in heat release power by enlargement of the heat exchange area inside the reactor with 270 to 300g TCHS material (anhydrous $CaCl_2$) [13]
(legend modified for better readability and translated from German)

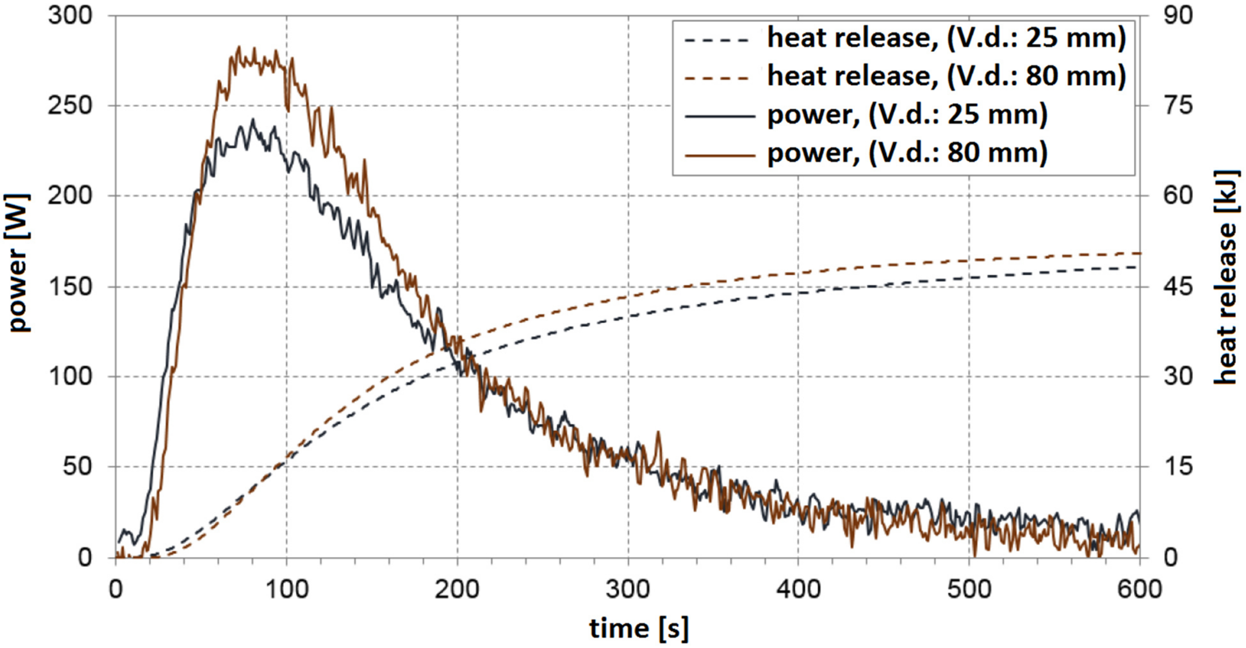

Figure 23: increase in heat release power by enlarged valve diameter between reactor and sorbate vessel with a TCHS material mass of 130g (anhydrous $CaCl_2$) [13]
(legend modified for better readability and translated from German)

The experimental data shown in Figure 22 was obtained with different reactor configurations containing between 270 to 300g of anhydrous $CaCl_2$ and 130g in Figure 23, yet both show peak power of around 300W. Figure 24 (left) shows the reactor configuration used for the experiments presented in Figure 22. Figure 24 (right) gives an overview of the reactor configuration (**only** the 7 tubes in the middle) used for the experiments presented in Figure 23.

Figure 24: different reactor configurations [13]

Figure 25 shows the reactor tubes with soldered fins that were in use for the experiments presented in Figure 23. This shows that despite the difference in TCHS material (more than twice the mass for Figure 22 compared to Figure 23), it is possible to achieve better peak power (325W vs. 275W). Optimized heat exchange characteristics due to an increased heat exchange area, achieved by the use of thin fins soldered to reactor tubes, allow for a better performance. It has to be stated that this level of manufacturing was achieved by an external manufacturer specialized in finned tubes. This shows how influential the size of a reactor's heat-exchange surface is, on its heat release performance.

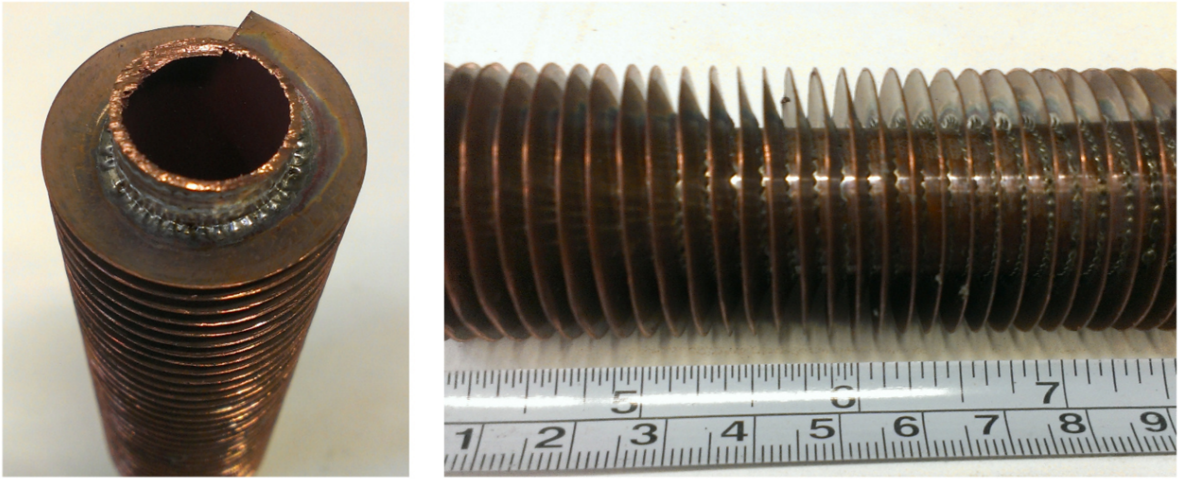

Figure 25: reactor tube with soldered fins [13]

3 Materials and methods

3.1 Test facility and TCHS reactor

An existing test bench was adapted to implement the TCHS system shown in Figure 26. The test bench consists of two separate coolant fluid circuits, where one can be heated by an electrical heating device and both can be cooled, using cold tap water and heat exchangers. A vacuum pump to evacuate the TCHS system is also part of the test bench. The existing TCHS system was replaced with a new TCHS system (Figure 26). The heatable coolant circuit is used to feed the water/coolant jacket around the reactor with hot coolant and the second coolant circuit is utilised to cool the sorbate condenser.

The new TCHS system consisted of a reactor (Figure 27) made out of copper for excellent thermal conductivity and corrosion resistance. The reactor was design in order to be small to test the cartridge design-idea but big enough to be fillable with TCHS material by hand. Fins were also included to increase the heat exchange surface between the TCHS material and the reactor as well as a one-piece design was chosen to minimise the potential for vacuum leaks. Due to manufacturing and handling restrictions (composite insertion into the grooves between the fins), the fins could not be made as thin and tightly spaced as shown in chapter 2.7. [46]

A removable sleeve was fabricated, that could be attached over the reactor, to hold a water/coolant coat in order to mimic engine coolant or oil flowing around the reactor. The additional parts of the TCHS system were standard parts out of vacuum and plumbing parts catalogues.

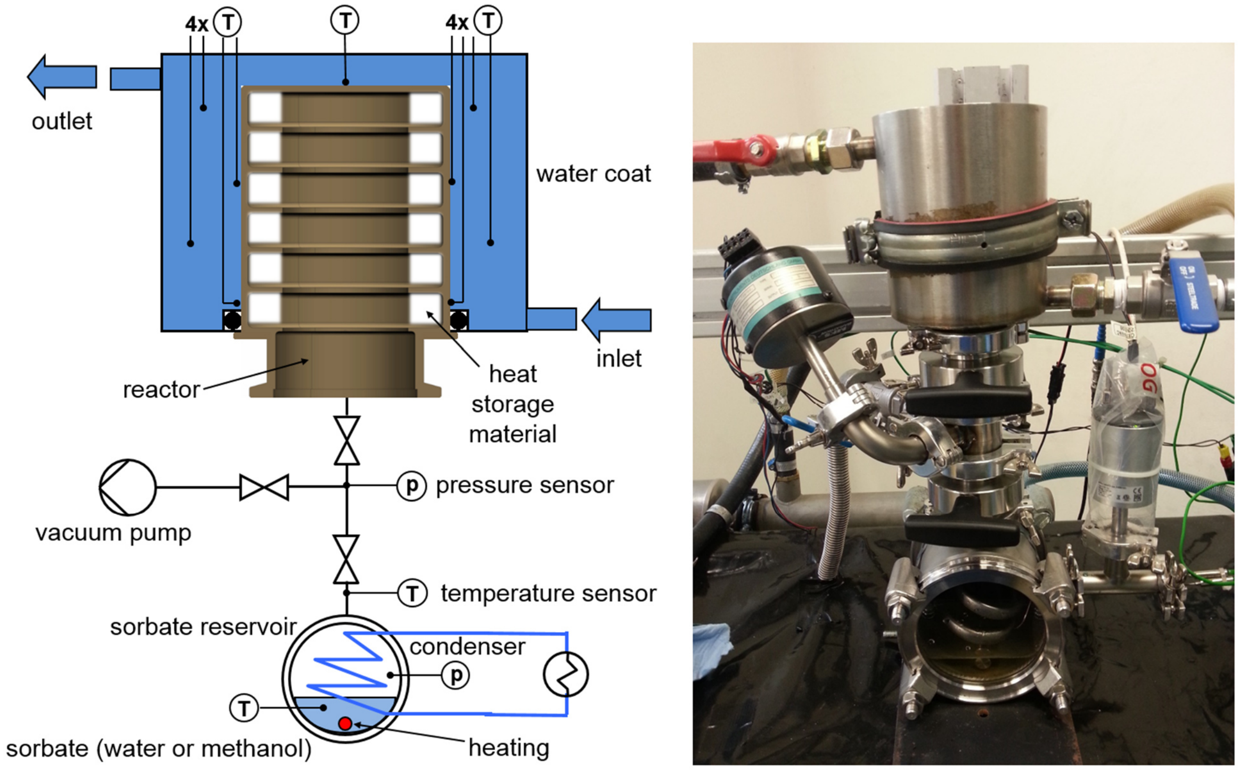

Figure 26: cartridge style TCHS system for experimental use [10]

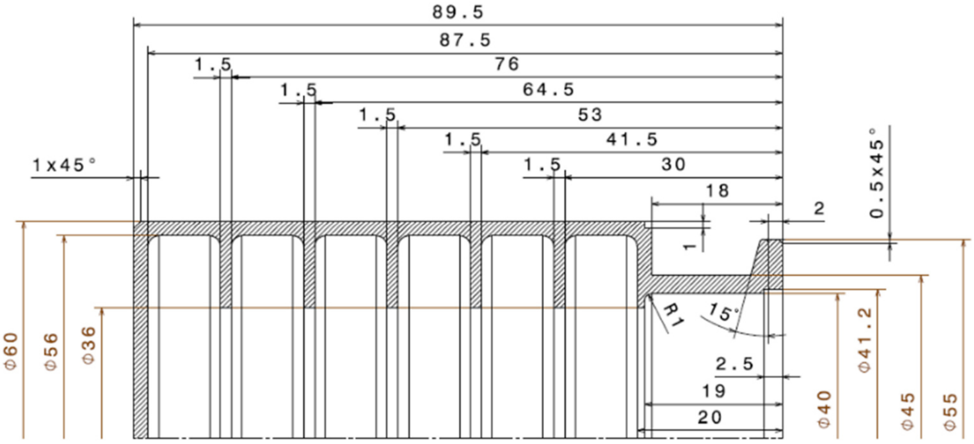

Figure 27: drawing of the TCHS reactor [10]

The data acquisition system consists of temperature sensors for the reactor surface as well as for the water jacket, sorbate reservoir (fluid and gaseous phase) and for the condenser temperature. Two pressure sensors are used to measure both reactor and sorbate reservoir pressures independently. A self-designed LabVIEW file takes care of data acquisition and visualization as well as operation of the test bench. The LabVIEW file provided flow control for coolant pumps as well as temperature control algorithms for controlling the temperature of the water/coolant coat around the reactor and of a small drying oven for TCHS material.

Linearization was used in order to calibrate the pressure sensor signals and adequate accuracy was achieved. Temperature sensors were implemented into the LabVIEW file using standard LabVIEW settings for type K thermocouples.

3.2 TCHS-composite base-materials

TCHS materials were obtained by *Sigma Aldrich* as well as glass wool, utilised as a carrier material to create a TCHS composite material. In addition, copper wool (STAX Cu99 M80) was used to form composites with better thermal conductivity, based on the better thermal conductivity of copper (371 W/mK) compared to glass (0.035-0.05 W/mK). [47], [48]

Figure 28 gives an overview of the materials in use, to create the investigated TCHS composites.

calcium cloride
$CaCl_2$

aluminium sulfate
$Al_2(SO_4)_3$

lithium bromide
LiBr

magnesium sulfate
$MgSO_4$

magnesium cloride
$MgCl_2$

STAX Copper wool
Cu99 M80

Glass wool
for laboratory use

Figure 28: materials in use to create TCHS composites [10]

3.3 Methods and experimental set-up

In order to conduct experiments, preparation work has to be done. Preparation of TCHS composites starts with a saturated aqueous solution of TCHS material (e.g. $CaCl_2$) which is used to soak the carrier material. Glass-wool-felt was cut to obtain small pieces respectively short glass wool fibres of about 2-4cm to create a material as non-directional as possible (amorphous), as suggested by Jakobi [13]. The glass wool was soaked for about 45 min before the material was put into a sieve (Büchner-funnel) connected to a vacuum pump via a side-arm flask in order to extract surplus solution out of the glass wool. Then wet composite was inserted manually into the reactor grooves. Composite using copper wool as carrier material was created by first inserting copper wool into the reactor grooves and then aqueous TCHS material solution was injected with a syringe, because of the poor absorption capacity of the copper wool.

For some experiments a novel method of TCHS composite construction was utilised. Before the reactor was filled with soaked glass wool, the reactor was mounted into a slowly turning lathe, filled with aqueous TCHS material solution and continuously heated with a heat gun in order to coat the inside homogenously with TCHS material. This was done in order to achieve a higher amount of TCHS material inside the reactor without using more glass wool and therefore decreasing the composite's vapour transport capability. Figure 29 displays the concept of a TCHS wall coating in combination with TCHS composite.

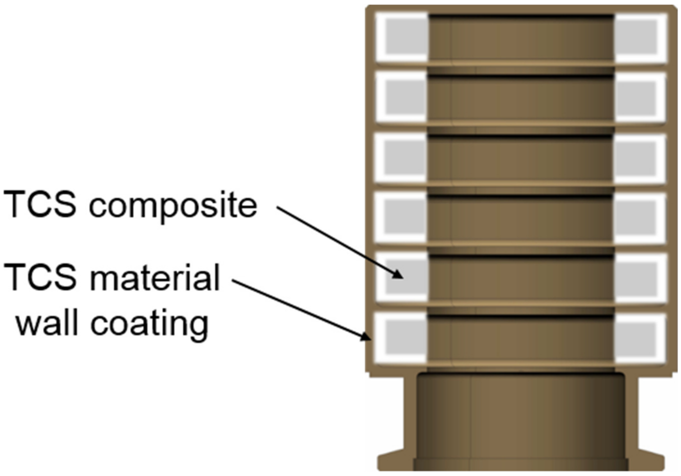

Figure 29: reactor profile sketch with TCHS wall coating and composite [10]

The thin wall coating (around 0.5 - 1mm) is intended to be thin enough to have good reaction kinetics and the composite above to be permeable enough to allow the sorbate vapour to reach the wall coating without much obstruction. In theory, this combines advantages of solid bed (e.g. maximum TCHS material per volume) and composite TCHS materials (e.g. enhanced vapour transport).

The loaded reactor was put into a LabVIEW-controlled oven (heat control and weight monitoring) and left to dry until no further weight loss was detected. To observe dehydration, the oven was put onto a scale and the weight decrease was recorded in order to determine if the dehydration was finished for the set dehydration temperature of 150°C.

The dehydrated reactor was then mounted into the testing rig and evacuated. After a cool down phase until room temperature was reached, the hydration experiment was started by opening two valves between the sorbate reservoir and the reactor. The weight of the reactor was measured before and after every hydration experiment to link the sorbate uptake of the TCHS material with the heat release measured.

After the heat release comparison tests (comparative tests) with all five TCHS materials ($MgCl_2$, $MgSO_4$, $CaCl_2$, $Al_2(SO_4)_3$ and LiBr) were completed, the heat release characteristics were evaluated.

Further experiments (continuative tests) were only conducted with TCHS materials, where a feasible heat release was observed. Methods for hydration and dehydration were adapted to further resemble the working conditions a TCHS cartridge-design reactor would experience, when implemented into a motor vehicle. Therefore, the dehydration method was changed to dehydration with the use of hot coolant (water/glycol mixture) at a temperature of 110°C, under evacuated reactor conditions (i.e. gaseous sorbate poses the only gaseous phase inside the TCHS device/reactor). 110°C was chosen to mimic elevated coolant temperatures, which were stated favourable for TCHS performance. [13]

Before the reactor received a new filling, it was cleaned in order to prevent contamination of the new TCHS material with traces from other TCHS materials.

3.4 Conducted experiments

After a start-up phase, where experiments with $MgSO_4$ were conducted in order to test the functionality of the TCHS system, a reference point in order to compare different TCHS materials and composite designs was established. $CaCl_2$ was used as a TCHS material to establish a reference point, because previous research has shown that $CaCl_2$ is a suitable TCHS material. [13]

Table 3 gives an overview of the conducted experiments in order to test different approaches to use $CaCl_2$ as a TCHS material in combination with the cartridge style reactor. Glass wool and copper wool composites were tested as well as the amount of glass wool used to fill the reactor was varied. Further a composite was tested where diluted aqueous TCHS material solution was used to impregnate glass wool and an experiment with an additional TCHS-material wall-coat on the inside walls of the reactor was performed.

Experiments were repeated until a representative result for this experiment was obtained, therefore maximum and minimum values of an experiment were not taken into account. The Results of heat-release experiments presented in this work are the representative results for each experiment variation, except it is stated differently.

The method that showed best heat release characteristic was to use 15g glass wool soaked in a saturated aqueous TCHS material solution and the use of an additional TCHS wall coating on the inside walls of the reactor. This method was then used to test the other TCHS materials: $MgSO_4$, $MgCl_2$, LiBr and $Al_2(SO_4)_3$.

Table 3: TCHS experiments with $CaCl_2$ to establish a reference value

Carrier material	TCHS material	Sorbate	Mass carrier [g]	Mass TCHS materials [g]	comment
Glass wool	$CaCl_2$	H_2O	15	15	composite
Glass wool	$CaCl_2$	H_2O	~15	~24	Wall coating and composite
Glass wool	$CaCl_2$	H_2O	40	56	composite
Copper wool	$CaCl_2$	H_2O	47,64	17,58	composite
Copper wool	$CaCl_2$	H_2O	47,64	48,02	Composite with extra TCHS material injected

Table 4 shows the further conducted experiments (comparative tests) to compare the other TCHS materials with $CaCl_2$. Those experiments were performed with sorption times of 60 min and desorption was done in an oven.

Table 4: heat release comparison tests

Carrier material	TCHS material	Sorbate	Mass carrier [g]	Mass TCHS m. [g]	comment
Glass wool	LiBr	H_2O	16	43	Wall coating and composite
Glass wool	LiBr	H_2O	16	43	Wall coating and composite, desorption with coolant
Glass wool	$Al_2(SO_4)_3$	H_2O	15	22	Wall coating and composite
Glass wool	$MgCl_2$	H_2O	15,6	25,34	Wall coating and composite
Glass wool	$MgSO_4$	H_2O	15,6	16,2	Wall coating and composite
Glass wool	$CaCl_2$	H_2O	~15	~24	Wall coating and composite

After all five TCHS materials were tested, the non-promising ones were left aside in order to examine the promising TCHS material candidates more thoroughly.

The second testing round (continuative tests) focussed on shorter sorption times (5 min instead of 60 min) and the comparison between water and methanol as sorbate, as well as desorption with the use of hot engine coolant (110°C) instead of an oven. Desorption times were also reduced to 30 min, to represent time restrictions for desorption, expected under real working conditions, for a TCHS device implemented into motor vehicles. Desorption was conducted under low pressure conditions, where only the sorbate's vapour pressure was present inside the TCHS system. Table 5 lists the different experiments undertaken during this round (continuative tests) of TCHS material experiments.

Table 5: conducted experiments with 5min sorption time and dehydration with hot coolant

Carrier material	TCHS material	Sorbate	Mass carrier [g]	Mass TCHS m. [g]	comment
Glass wool	$CaCl_2$	H_2O	15,8	31,7	Wall coating and composite
Glass wool	$CaCl_2$	H_2O	15,8	31,7	Wall coating and composite, heat release to coolant
Glass wool	$CaCl_2$	Methanol	15,8	31,7	Wall coating and composite
Glass wool	$CaCl_2$	Methanol	15,8	31,7	Wall coating and composite, heat release to coolant
Glass wool	LiBr	H_2O	15,7	33,5	Wall coating and composite
Glass wool	LiBr	Methanol	15,7	33,5	Wall coating and composite
Glass wool	$MgCl_2$	H_2O	15,7	26,77	Wall coating and composite
Glass wool	$MgCl_2$	Methanol	15,7	26,77	Wall coating and composite

Due to time restrictions, LiBr and $MgCl_2$ sorption experiments were performed only without the use of the water/coolant jacket during heat release experiments.

3.5 Experiment evaluation

Experiment evaluation was done using the measured and logged temperature, pressure and weight signals. An Excel template was created to visualize the logged temperature profiles and calculate e.g. the released power during hydration.

To calculate the power of heat release, the relative high passive mass of the reactor (compared to the active mass of the TCHS composite) was beneficial because it allowed for a sufficient heat uptake from the TCHS composite without experiencing exceedingly high temperature increases. This led to a good measurability of the temperature increase during heat release as well as providing a good heat flow from the composite into the reactor, keeping the composite relatively cool, which is assumed to help in terms of sorption performance.

Main focus during evaluation of the experiments was on the achieved heat release power of each composite. To calculate heat release power, the mass of the reactor and the heat capacity of the reactor material as well as the temperature rise per second were used, as shown in Equation (7)

$$P = m_{reactor} * c_{p-reactor} * (\vartheta_{t+1} - \vartheta_t) \tag{7}$$

Equation (7): calculation of heat release power

$m_{reactor}$	passive mass of the reactor [kg]
$c_{p\text{-}reactor}$	heat storage capacity of the reactor material (copper) [J*kg^{-1}*K^{-1}]
$\vartheta_{t+1} - \vartheta_t$	temperature increase of the reactor material per second [°C*s^{-1}]
P	heat release power [W]

Because of the fixed reactor mass and heat capacity, heat release power depends exclusively on the speed of the temperature increase, the faster the temperature increases the higher the heat release power becomes.

4 Results

4.1 Preliminary tests / reference point

Figure 30 up to Figure 34 shows the achieved results with different TCHS-composite preparation-methods. Temperature rise as well as heat release power and a view inside the reactor filled with composite are given for each composite variation.

Figure 30 shows the results for the reactor filled with composite consisting of 15g dry glass wool soaked in saturated $CaCl_2$ solution.

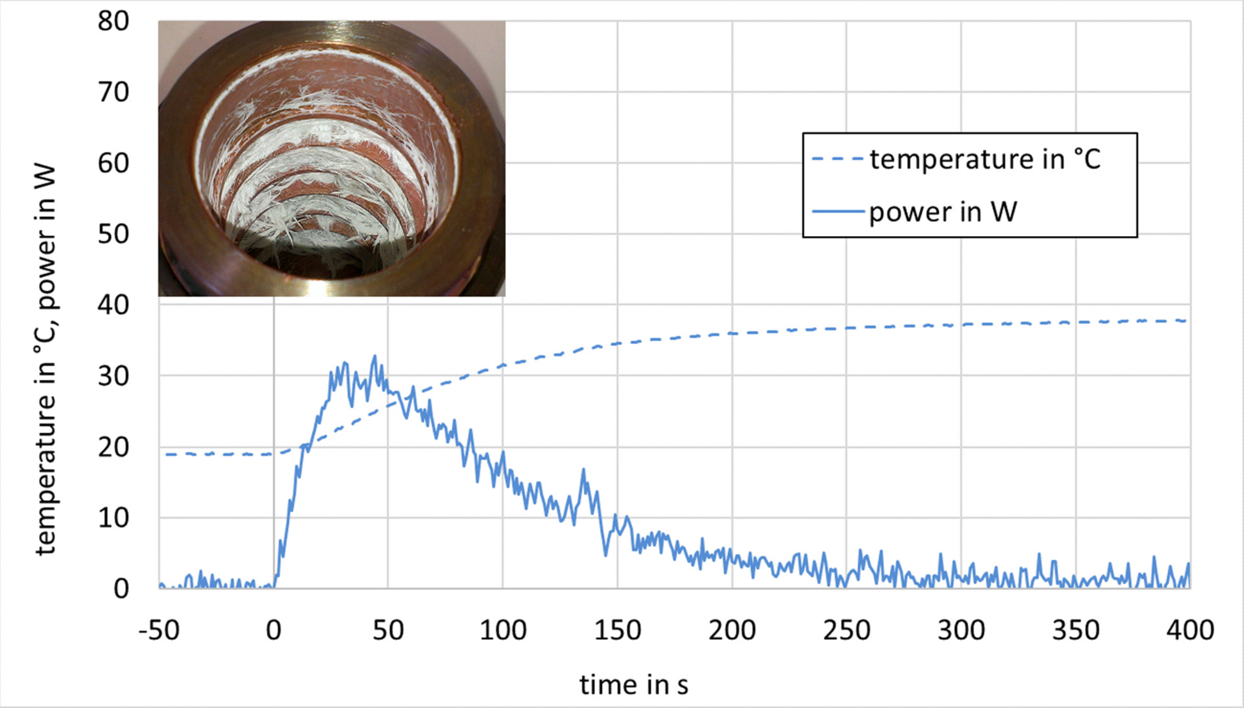

Figure 30: 1) Reactor filled with composite (15g dry glass wool mass soaked in saturated $CaCl_2$ solution)

Figure 31 shows the heat release characteristic for the composite variation ($CaCl_2$ wall coating plus composite consisting of 15g dry glass wool and $CaCl_2$) with the best heat release power and heat release after 300s. In blue an average heat release characteristic of this composite variation is given and in red the best heat release characteristic observed for this composite variation is given, to show the potential capabilities of this composite variation.

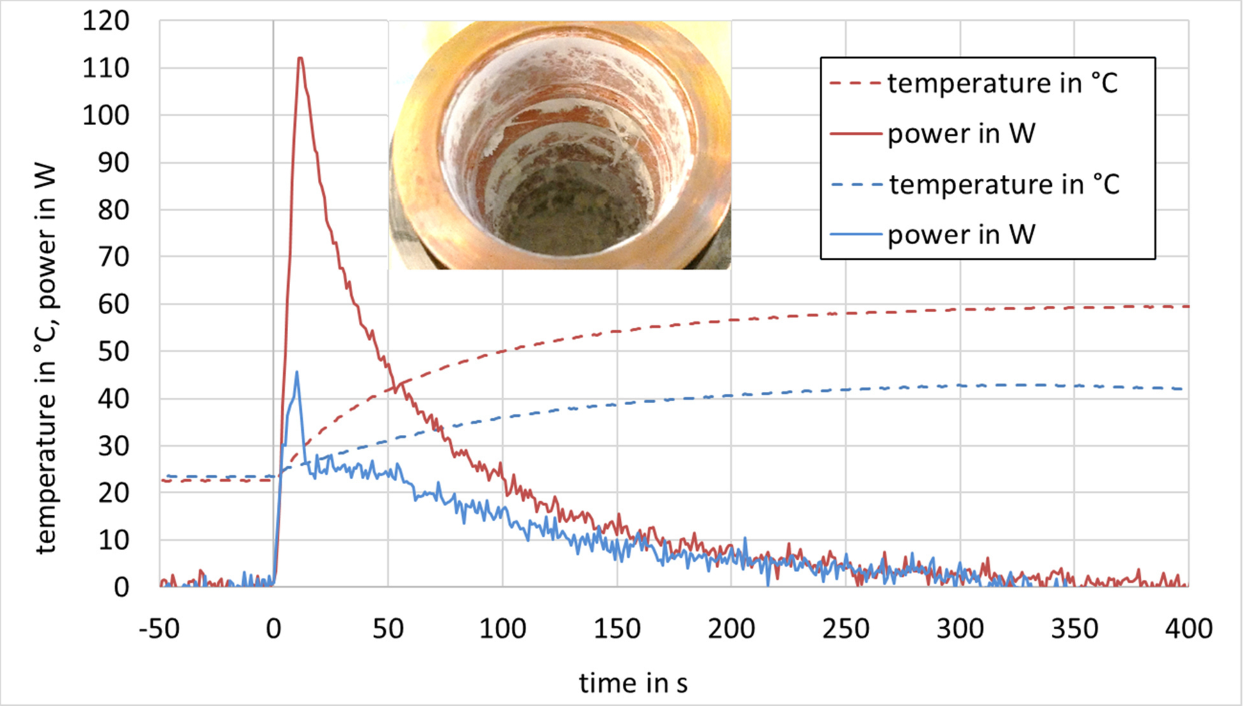

Figure 31: 2) Reactor coated on the inside wall with $CaCl_2$ & filled with composite (15g dry glass wool mass soaked in saturated $CaCl_2$ solution)
blue: average heat release characteristic for this composite variation
red: best heat release characteristic for this composite variation

Figure 32 gives the results for the reactor coated on the inside wall with $CaCl_2$ and filled with composite, with increased glass wool mass (40g dry glass wool mass soaked in saturated $CaCl_2$ solution).

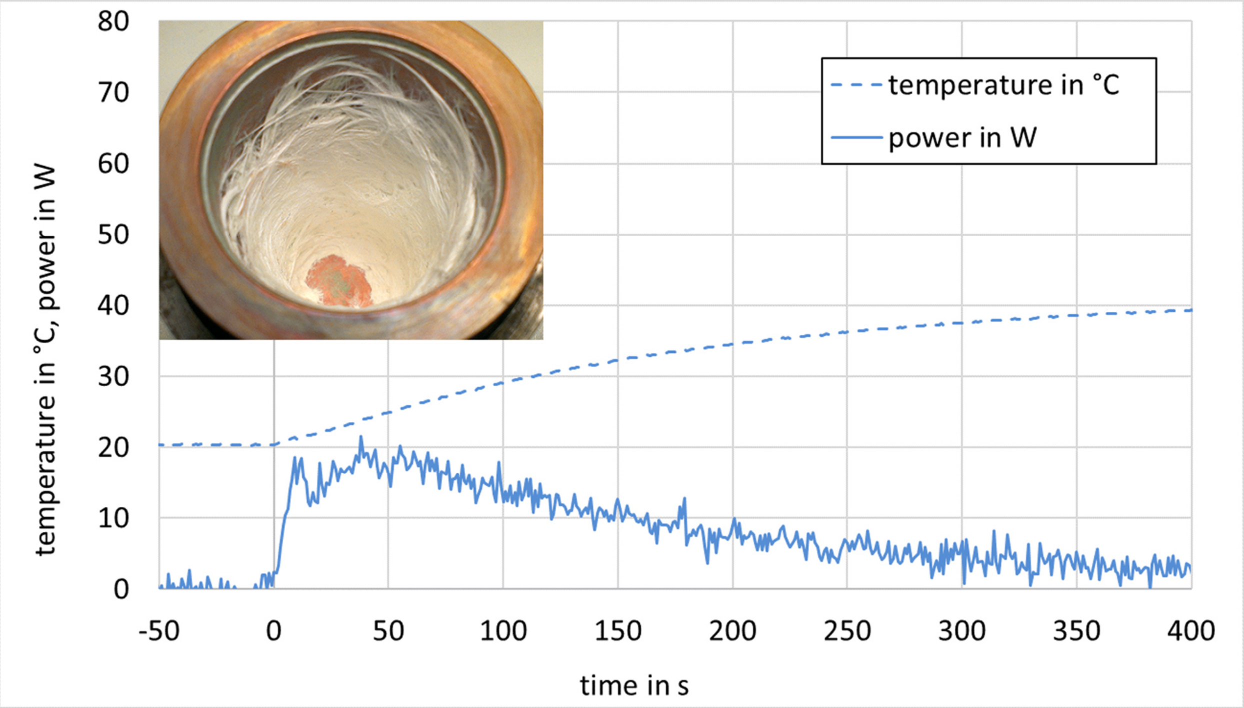

Figure 32: 3) Reactor coated on the inside wall with $CaCl_2$ & filled with composite; increased glass wool mass (40g dry glass wool mass soaked in saturated $CaCl_2$ solution)

Figure 33 and Figure 34 present results for a reactor filling consisting of copper wool based composite with two different $CaCl_2$ contents.

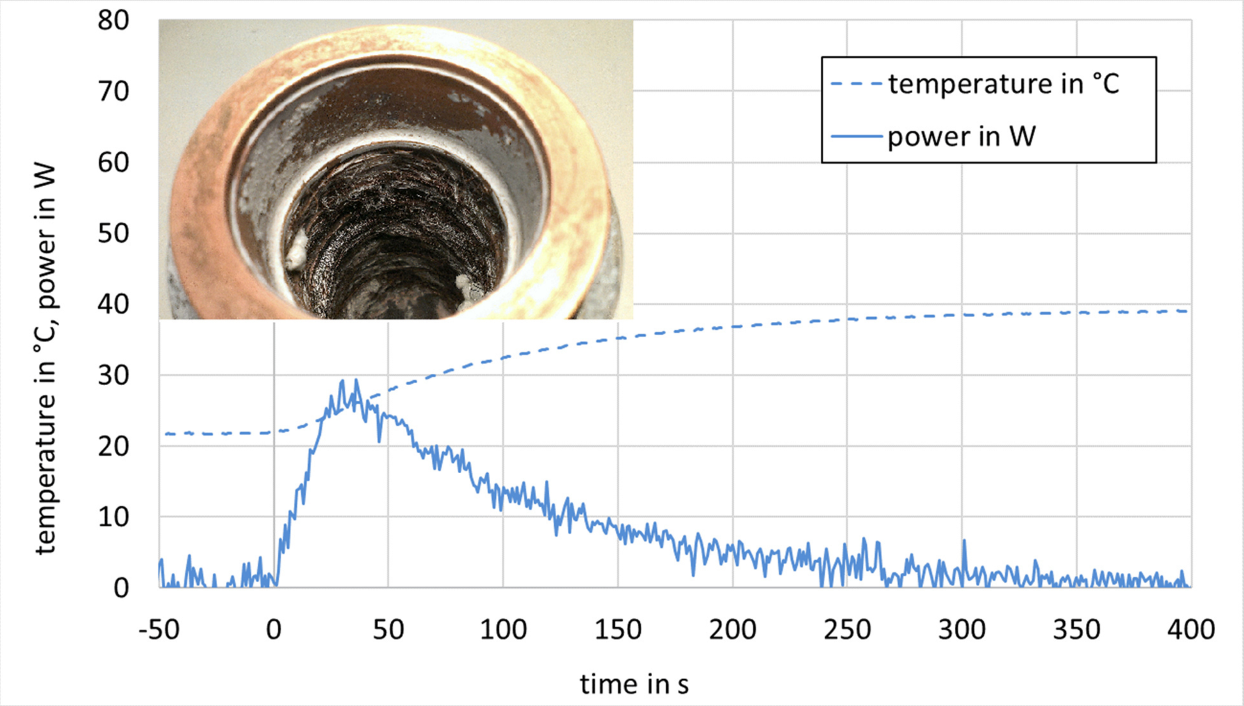

Figure 33: 4) Reactor filled with copper-wool composite

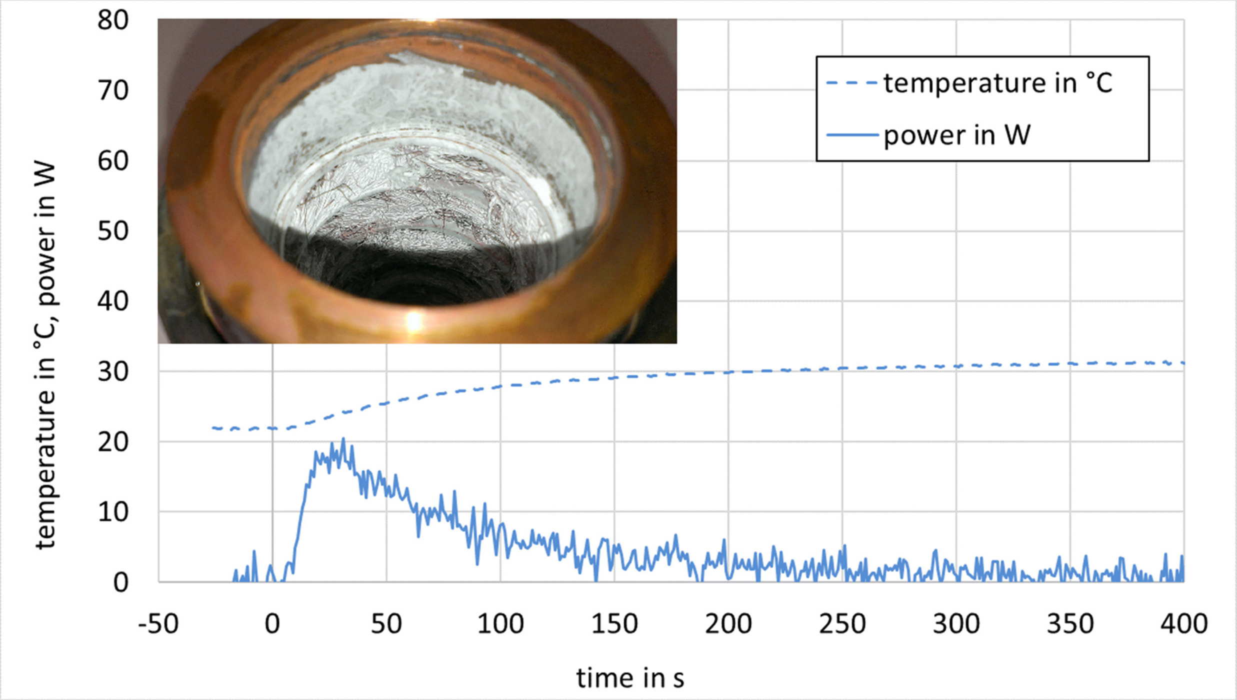

Figure 34: 5) Reactor filled with copper-wool composite with additional $CaCl_2$

An overview of the experiment results from TCHS experiments with $CaCl_2$ composites and water as sorbate (preliminary tests), in order to find a reference point for comparative testing of TCHS materials, is given in Table 6.

The experiment shown in Figure 31 (blue) shows the best heat release characteristics in terms of peak heat-release-power and total released heat after 300s sorption time. The utilised reactor filling consists of a TCHS-material ($CaCl_2$) wall-coating on the inside of the reactor and an additional composite filling, consisting of 15g dry glass wool soaked in saturated $CaCl_2$ solution.

Table 6: experiment results of reactor-filling-method evaluation with different $CaCl_2$ composites (Figure 30 to Figure 34)

test	**peak power**	**power 30s**	**total energy (300s)**	**$CaCl_2$ Content**	**spec. power 30s**	**spec. total energy**
1) Reactor filled with composite	30W	22W	3408J	15g	1,47 W/g	227J/g
2) Reactor coated on inside wall & filled with composite	45W	31W	3631J	32g	0,97 W/g	113J/g
3) Reactor coated on inside wall & filled with composite, Increased glass wool mass	20W	16W	3208J	56g	0,29 W/g	57J/g
4) Reactor filled with copper wool composite	30W	22W	3195J	18g	1,2 W/g	177J/g
5) Reactor filled with copper wool composite, additional $CaCl_2$	20W	15W	1685J	48g	0,31 W/g	35J/g

In addition to that the second experiment shown in Figure 31 (red) shows the strong potential this reactor filling method has. In combination with the second experiment shown in Figure 31 (blue), presenting an average heat release performance of this reactor filling, this reactor filling method was chosen to compare the remaining TCHS materials.

4.2 $CaCl_2$

Comparative tests

Figure 35 shows the heat release characteristic of $CaCl_2$ and gives a visual impression of the composite filled reactor. $CaCl_2$ shows a peak heat release power of 45W, a temperature difference of 19.45°C and a sorbate uptake of around 6g of water. $CaCl_2$ glass wool composites are white in colour and show only minor signs of colour change during repeated use, therefore no immediate corrosive behaviour was observed.

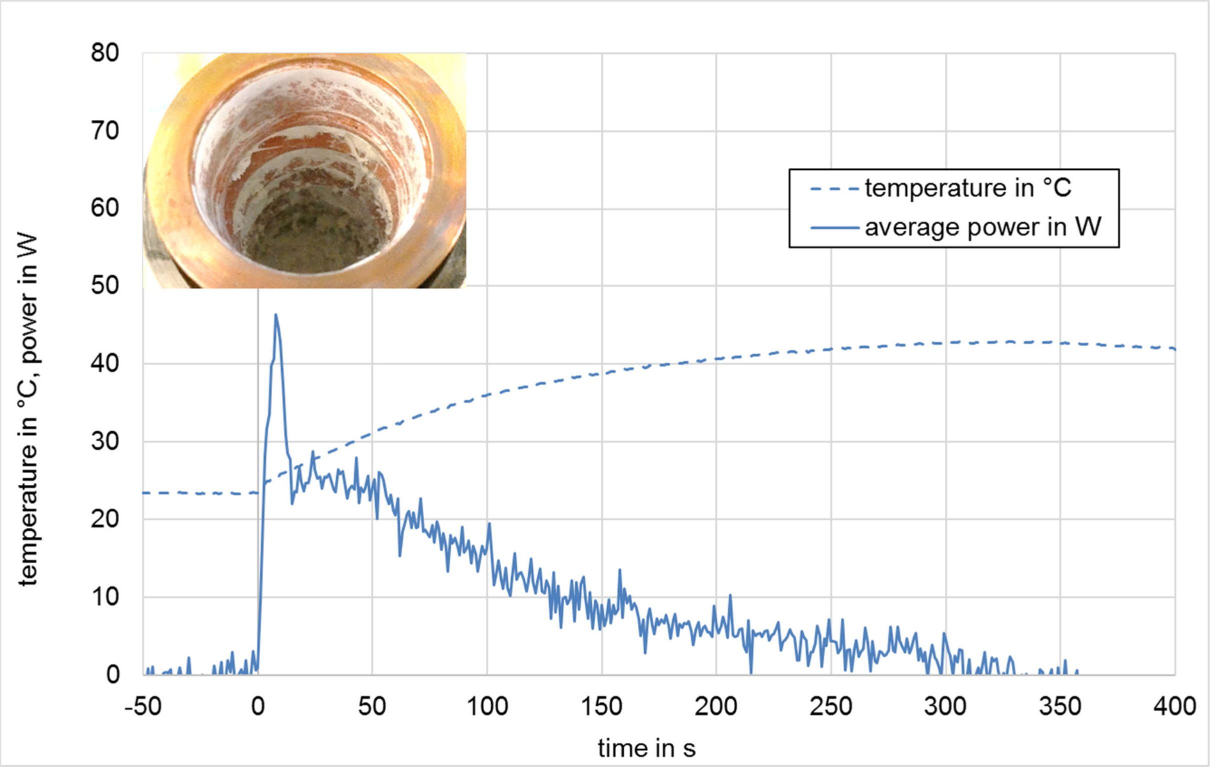

Figure 35: heat release of $CaCl_2$ incl. view inside the reactor

Continuative tests

Continuative tests with $CaCl_2$ under vehicle specific operation conditions described in chapter 3.4 with water as sorbate showed, that after a complete desorption at 150°C in an oven to gain a repeatable starting point, heat release and sorbate uptake decreased slightly for every sorption/desorption cycle. In addition, desorption for 30 min with 110°C did not prove feasible to remove the sorbate. Therefore, the mass balance of the TCHS composite was positive (gaining weight) for every sorption/desorption cycle. Data shows that desorption (30 min at 110°C) starts to become effective at increased water load (monohydrate $CaCl_2$) of the TCHS composite, but only removing 60% of the sorbate uptake of one sorption phase (5 min). This corresponds with the literature cited in chapter 2.4.1.

Subsequently sorbate was changed to methanol in order to test a potential sorbate material for cold weather application, because of the low freezing point of methanol (-97.88°C). [49]

The use of methanol as sorbate showed an improved sorption characteristic, in a way that heat release power increased from 20W to 25W peak heat-release-power as shown in Figure 36. Desorption characteristic improved as well. Desorption for 30 min and 110°C was now able to remove all sorbate uptake after each sorption run, therefore maintaining a neutral mass balance for the TCHS composite, keeping it fully charged.

For both methanol and water as sorbate, the relative sorbate uptake during sorption experiments (5 min) was roughly the same with 0.37 mol_{H2O}/mol_{CaCl2} for water and 0.34 $mole_{methanol}/mole_{CaCl2}$ for methanol.

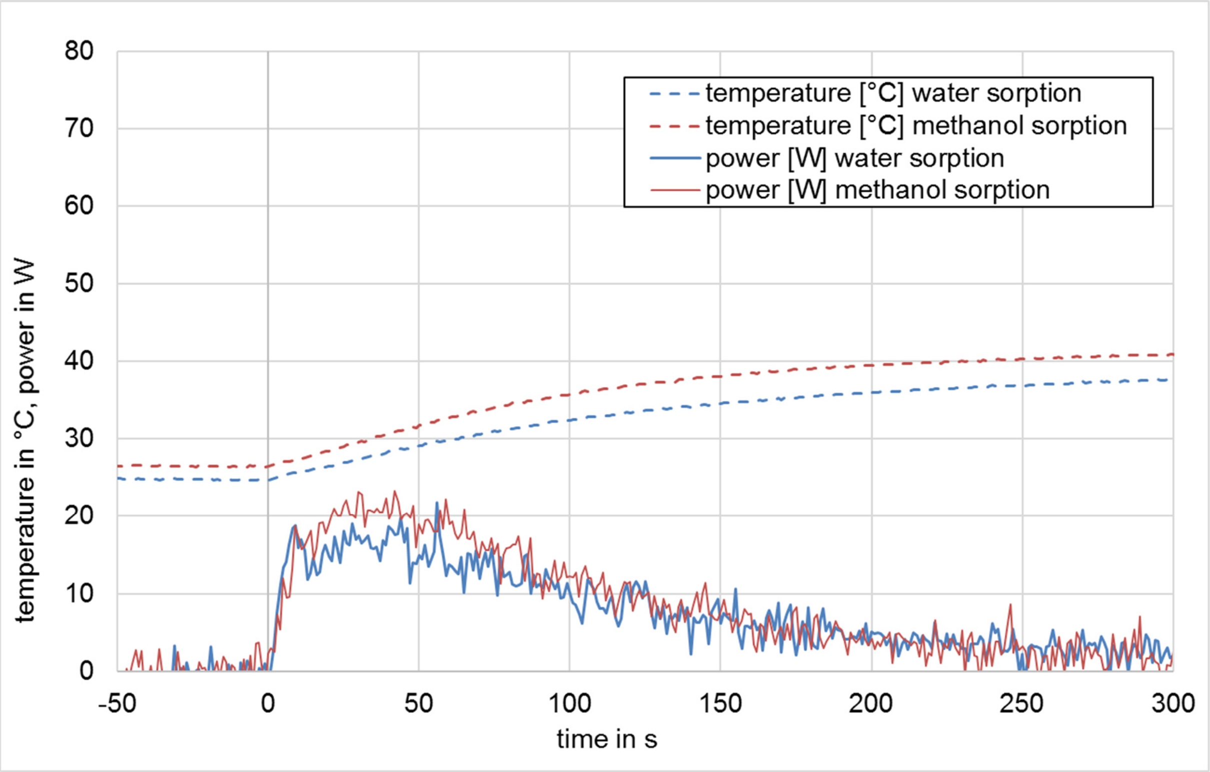

Figure 36: water and methanol sorption of $CaCl_2$ composite in comparison

The $CaCl_2$ composite containing 31.5g anhydrous $CaCl_2$ achieved a total heat release energy after 300s of sorbate sorption of 2420J for water as sorbate and 2721J for methanol as sorbate.

On rare cases, for both methanol and water as sorbate, “overachieving” sorption runs were experienced, where heat release power and sorbate uptake were greater than on other sorption runs with that specific reactor filling. This shows that composite reaction kinetics seem to undergo transformation processes during use.

After 14 sorption/desorption cycles with water and methanol, the $CaCl_2$ composite filling shows to have caused the copper reactor to corrode. The change in colour on the contact areas of $CaCl_2$ and copper, seen between Figure 35 and Figure 37, indicates corrosive properties of $CaCl_2$. The composite in the reactor grooves itself still remains white which indicates low mobility of the corrosion process and/or corrosion products.

Figure 37: view inside the reactor after 14 use cycles (sorption/desorption)

Due to time constraints, $CaCl_2$ was the only material where heat release experiments were conducted with the use of a coolant jacket around the reactor as shown in Figure 26. This led to increased heat flow through the reactor material into the coolant (being at ambient temperature, around 20°C) and therefore lowering the reactor and composite temperature compared to heat release experiments conducted with the reactor covered in insulation. For both sorbates (water and methanol) the lowered temperatures due to additional passive mass, realised by the reactor covered in coolant, led to increased sorbate uptakes of 23% for water and 32% for methanol as sorbate.

4.3 $MgSO_4$

Comparative tests

$MgSO_4$ composite shows low temperature increase (5.5°C), sorbate uptake (H_2O) and peak power as shown in Figure 38, compared to other TCHS materials like $CaCl_2$. $MgSO_4$ was also tested with methanol as sorbate but showed marginal sorbate uptake and temperature increase (0.6°C).

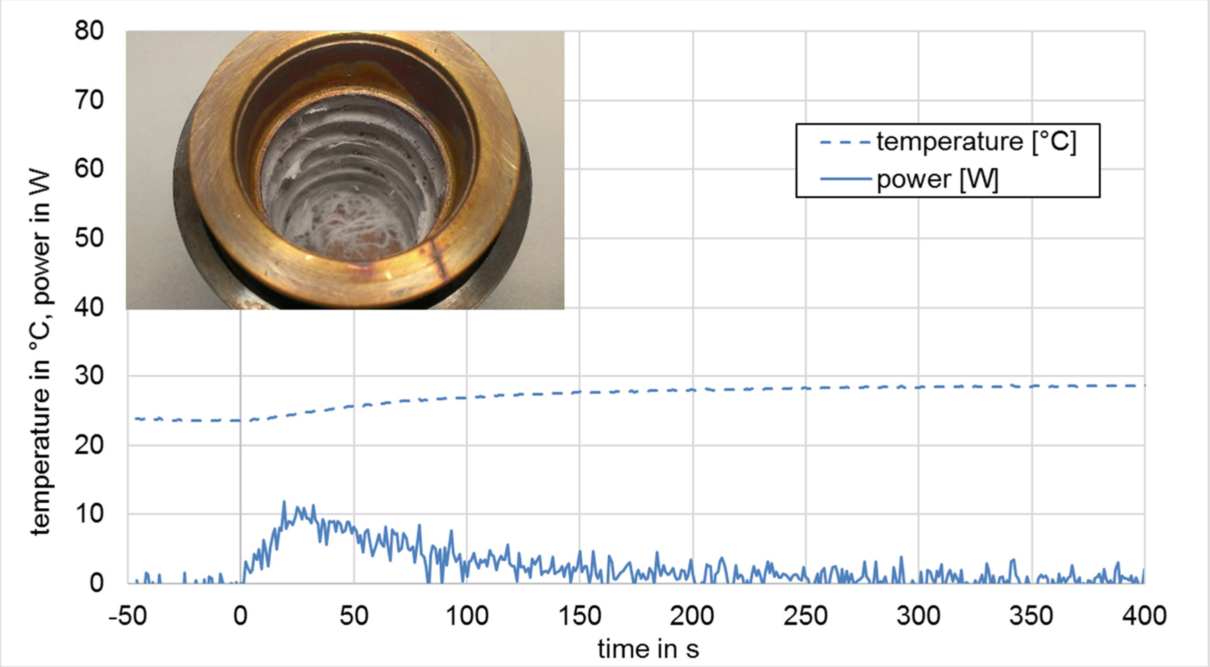

Figure 38: $MgSO_4$ composite heat release properties and view inside the reactor filled with composite

Continuative tests

Because of disappointing heat release characteristics in terms of peak power, despite promising properties of $MgSO_4$ in terms of energy density and desorption temperatures shown in chapter 2.4.2 and Figure 10, continuative tests with $MgSO_4$ were considered to be not productive.

4.4 $Al_2(SO_4)_3$

Comparative tests

Figure 39 shows the heat release and temperature increase for $Al_2(SO_4)_3$ composite with H_2O as sorbate. A maximum temperature increase of 3.4°C was experienced with a very low heat release peak power of roughly 3-4W.

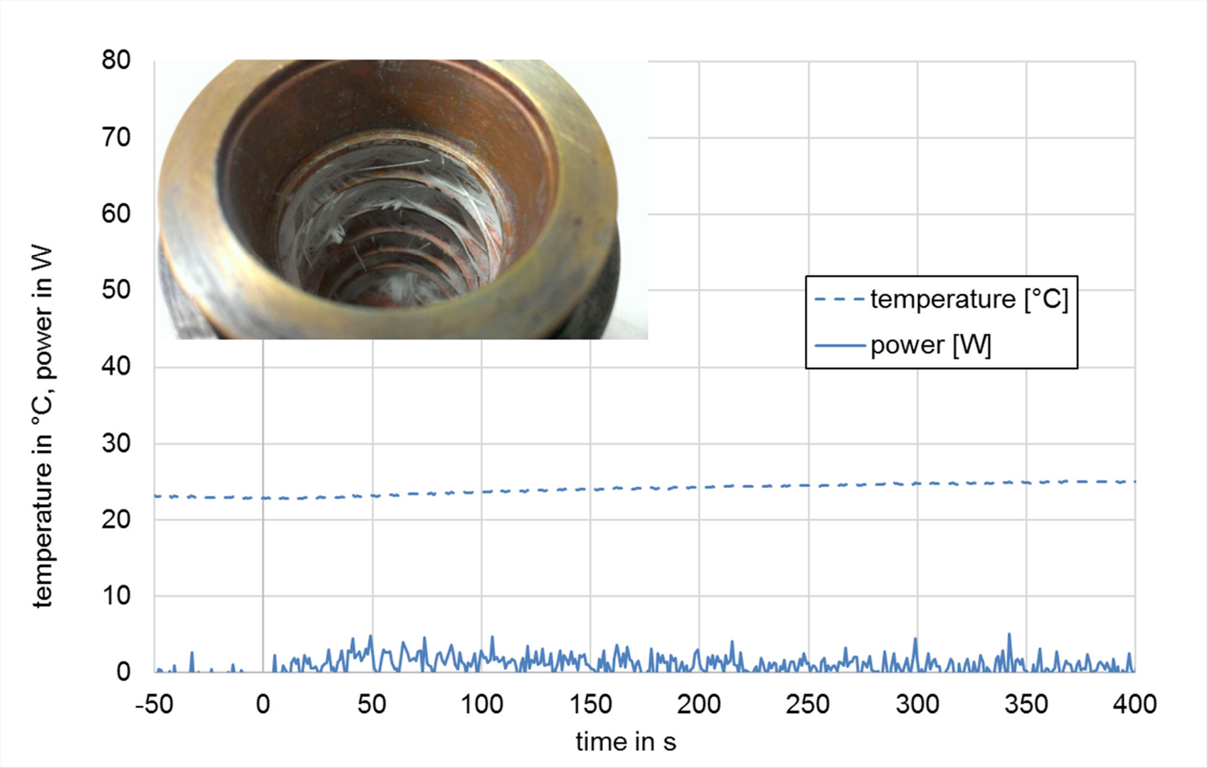

Figure 39: $Al_2(SO_4)_3$ composite heat release properties and view inside the reactor incl. composite

Continuative tests

No further tests were conducted for $Al_2(SO_4)_3$ composite because of low peak heat release power during sorption of H_2O.

4.5 LiBr

Comparative tests

Figure 40 shows promising heat release characteristics of LiBr composite for water absorption. Peak power reached 40W and a temperature increase of 25°C was measured. Sorbate uptake (H_2O) over one hour was 9.98g. LiBr showed to be very corrosive against copper as intense staining of the reactor and composite suggests.

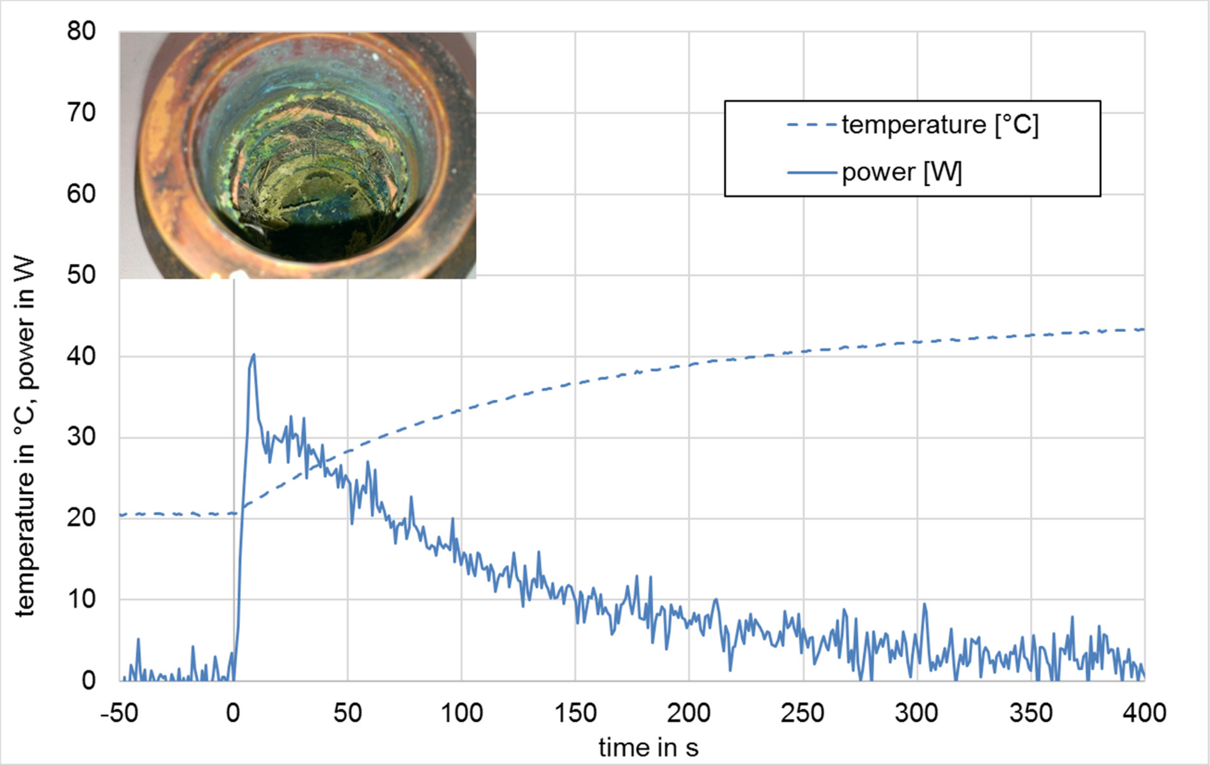

Figure 40: LiBr composite heat release properties and view inside the reactor filled with composite

Figure 41 gives an impression of the corrosiveness of LiBr against copper. The two pictures show the rapid development of corrosion during a 24h period. Figure 41 a) reveals that during initial drying of wet composite first signs of corrosion appear and Figure 41 b) shows the increase of corrosion 24h and one sorption experiment after Figure 41 a). Over a period of 6 days the corrosion process dissolved 5g copper out of the reactor material, this corresponded with roughly 1% of total reactor mass.

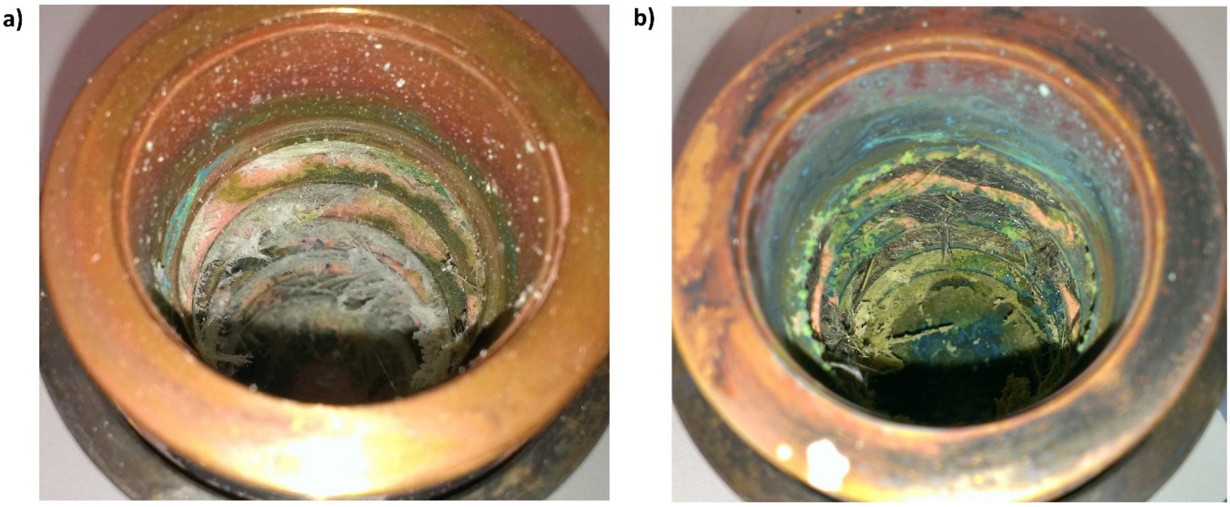

Figure 41: LiBr corrosion comparison: a) corrosion during initial desorption cycle right after new LiBr composite was filled into the reactor b) corrosion after one sorption cycle with the LiBr composite and 24h after picture a)

Continuative tests

Continuative tests with LiBr composite showed better overall characteristics of LiBr composite for methanol sorption than for H_2O sorption. Main difference between H_2O and methanol as sorbate was the poor desorption characteristic of LiBr with H_2O as sorbate, compared to methanol as sorbate. For H_2O as sorbate, desorption did not start until a cumulative H_2O uptake of 7.14g over 3 sorption cycles was reached, based on a dehydration level reached with an oven temperature of 150°C. Then desorption (110°C for 30 min) was only able to remove 1.8g of 3g H_2O, the LiBr composite absorbed during the latest sorption run.

Figure 42 shows the difference of the heat release with H_2O and methanol as sorbate. Blue curves show the sorption run with water as sorbate, after desorption of water became feasible (after a cumulative H_2O uptake of 7.14g). Methanol as sorbate showed excellent desorption characteristics as desorption could remove the sorbate completely after every sorption run.

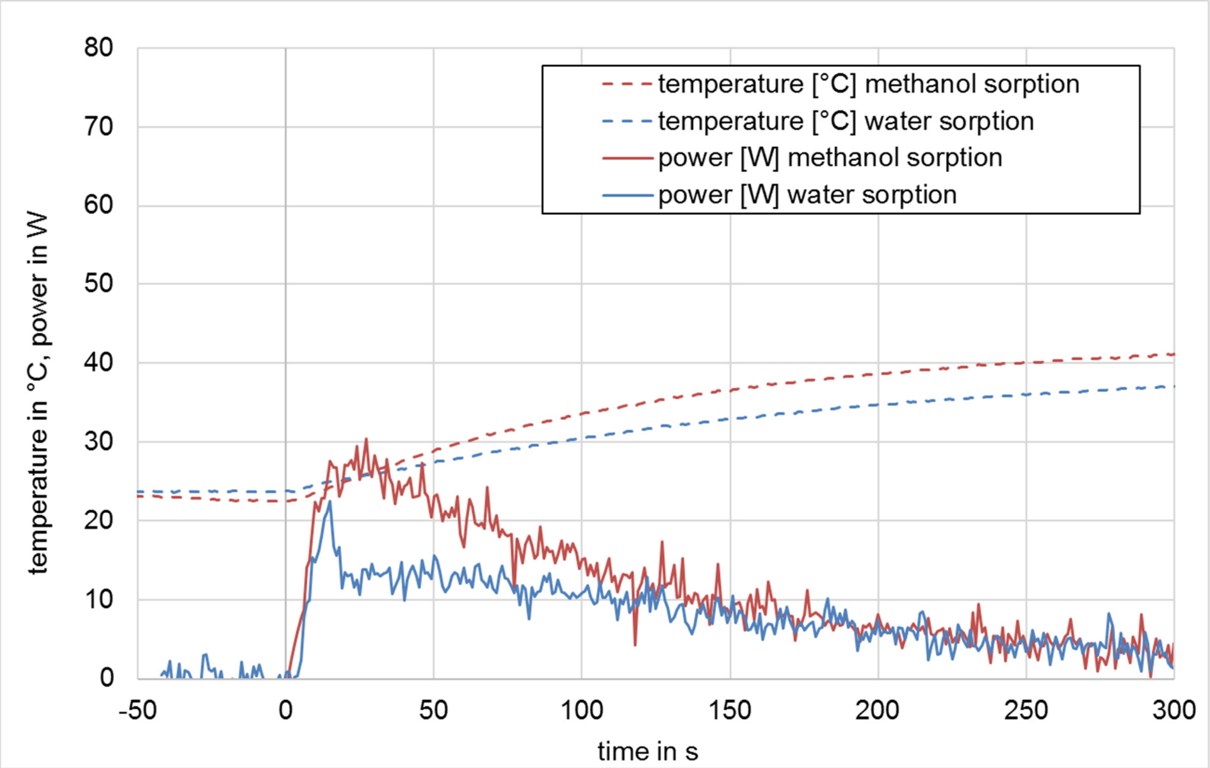

Figure 42: water and methanol sorption of LiBr composite in comparison

In comparison (Figure 42), methanol as sorbate leads to a higher peak power (30W) than water (22W) as sorbate, when compared under the working conditions established for the continuative tests. The hydration step (amount of sorbate molecules absorbed) for water

(0.46 $mole_{H2O}/mole_{LiBr}$) and methanol (0.48 $mole_{methanol}/mole_{LiBr}$) is similar. Total heat release, of the LiBr composite containing 33.5g dehydrated LiBr, after 300s of sorption was 2471J for water as sorbate and 3490J for methanol.

Strong corrosion of copper remained a problem with LiBr composite.

4.6 $MgCl_2$

Comparative tests

The heat release characteristic of $MgCl_2$ shown in Figure 43 indicates that $MgCl_2$ is a feasible material for TCHS. $MgCl_2$ composite shows a peak power of around 41W and a temperature increase of 22.2°C. The composite showed almost no change in colour, but on the contact area between composite and reactor (copper) a colour change (white to yellow) was observed which did not diffuse significantly into the composite.

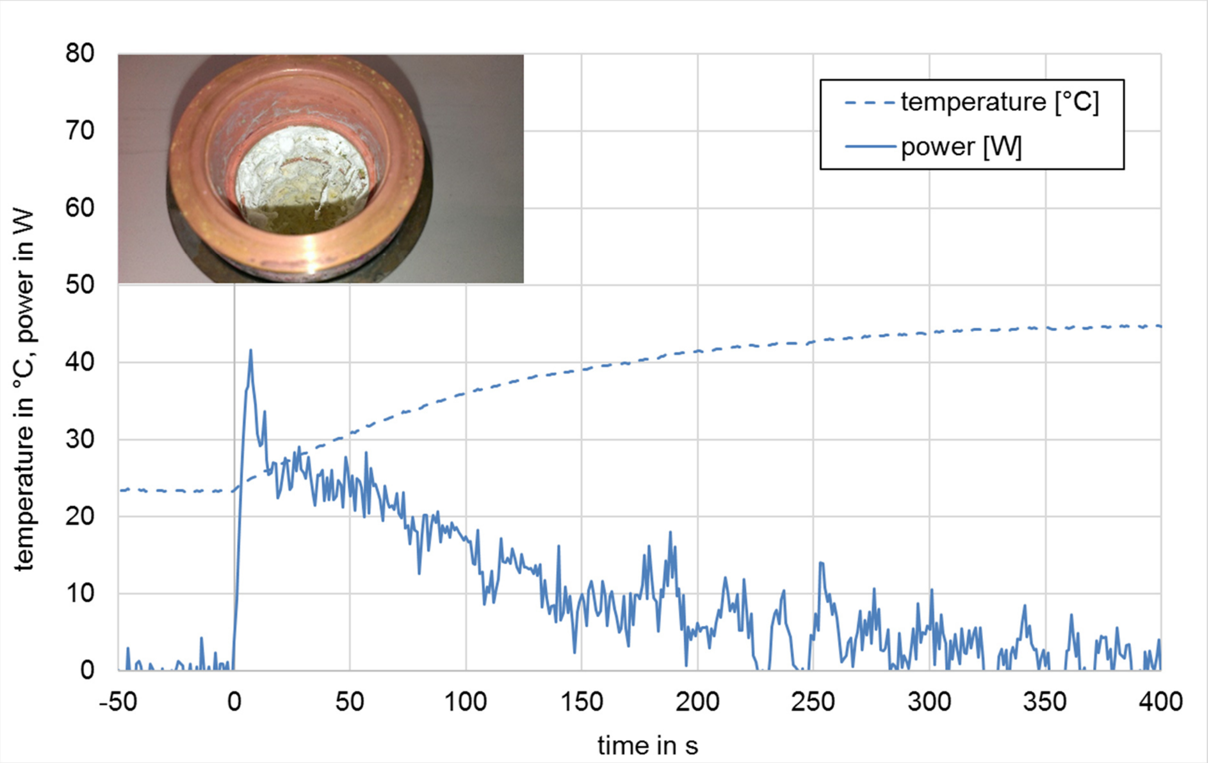

Figure 43: $MgCl_2$ composite heat release properties and view inside the reactor incl. composite

Continuative tests

Figure 44 presents a comparison of heat release and temperature rise of $MgCl_2$ composite with water (blue) and methanol (red) as sorbate. The use of methanol shows a higher peak power of released heat but a lower temperature increase.

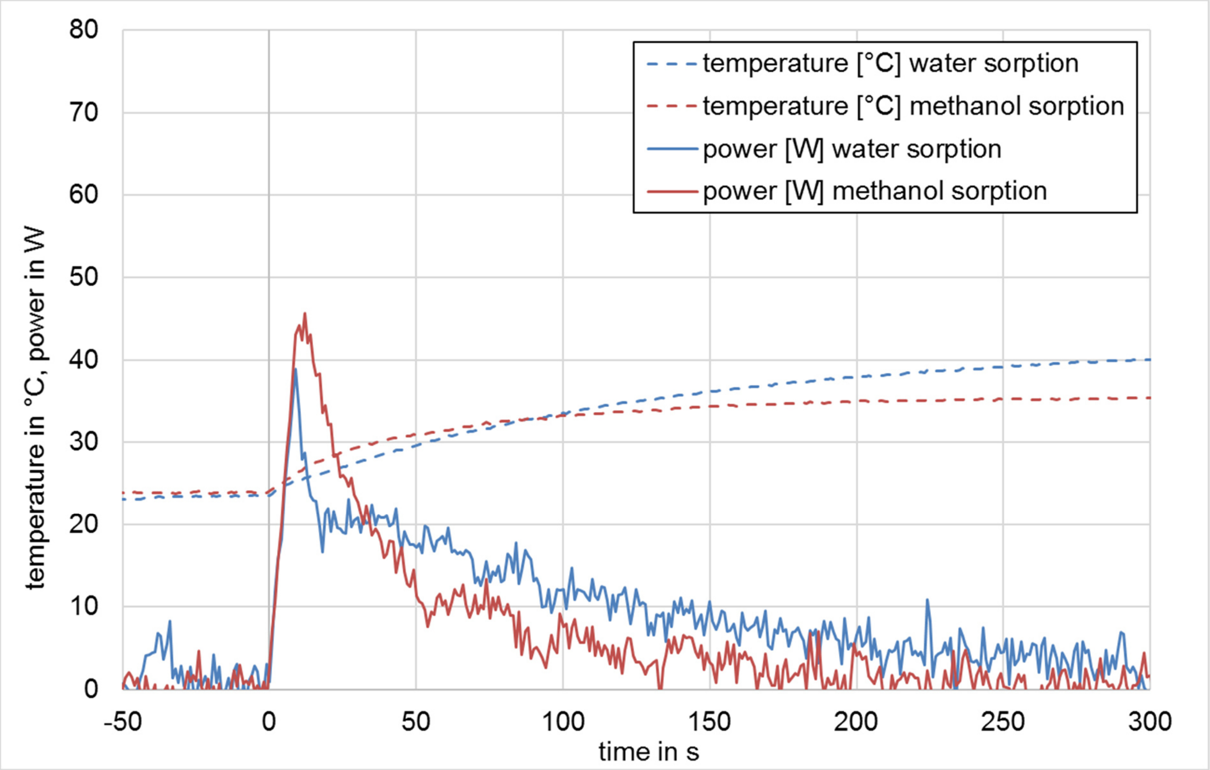

Figure 44: water and methanol sorption of $MgCl_2$ composite in comparison

The achieved hydration, of the $MgCl_2$ composite containing 27g anhydrous $MgCl_2$, for H_2O as sorbate was 0.55 $mole_{H2O}/mole_{MgCl2}$ and for methanol as sorbate 0.39 $mole_{methanol}/mole_{MgCl2}$. Peak power for methanol as sorbate was 45W with a total heat release energy after 300s of sorption of 2152J. $MgCl_2$ composite with water as sorbate reached a peak power of 40W with a total released energy after 300s of 3077J.

Desorption of $MgCl_2$ showed, that while using water as sorbate, the composite lost around 40% of the sorbate uptake of the latest sorption run during desorption. With the use of methanol, desorption (110°C for 30min) was more efficient, because desorption was able to remove almost all methanol uptake from the composite.

Figure 45 displays the colour change that occurred at the contact areas between the composite and the reactor over a period of 7 sorption/desorption cycles. The estimated reactor material (copper) loss was around 0.5g.

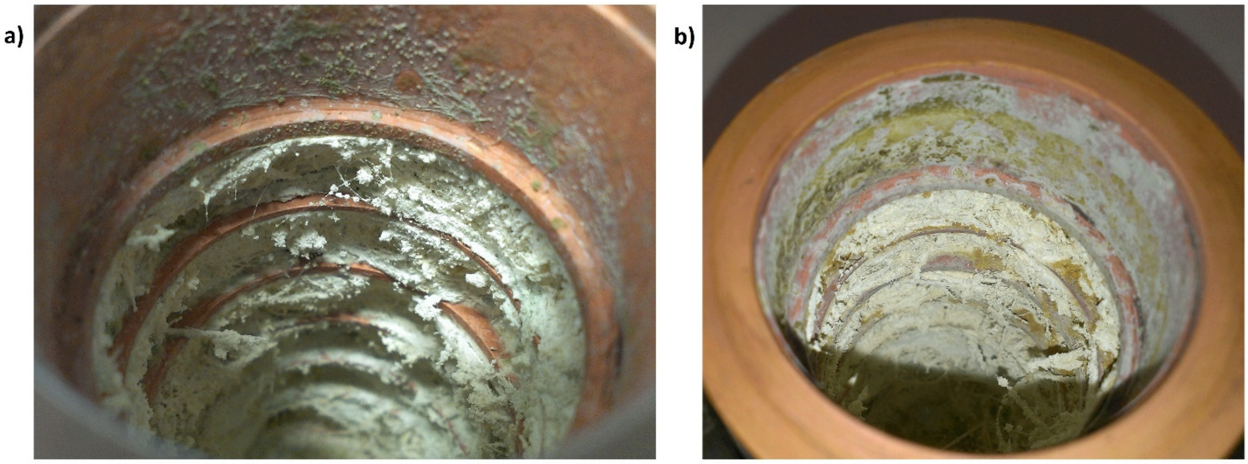

Figure 45: $MgCl_2$ composite: a) after initial drying of new reactor filling ($MgCl_2$ composite) b) after 7 sorption/desorption cycles of the $MgCl_2$ composite

4.7 Heat loss estimation

Figure 46 shows the heat loss through the reactor insulation during sorption experiments. The data presented in Figure 46 were obtained by monitoring the cooling rate of the previously externally heated reactor (with an oven) while being implemented into the full experiment setup.

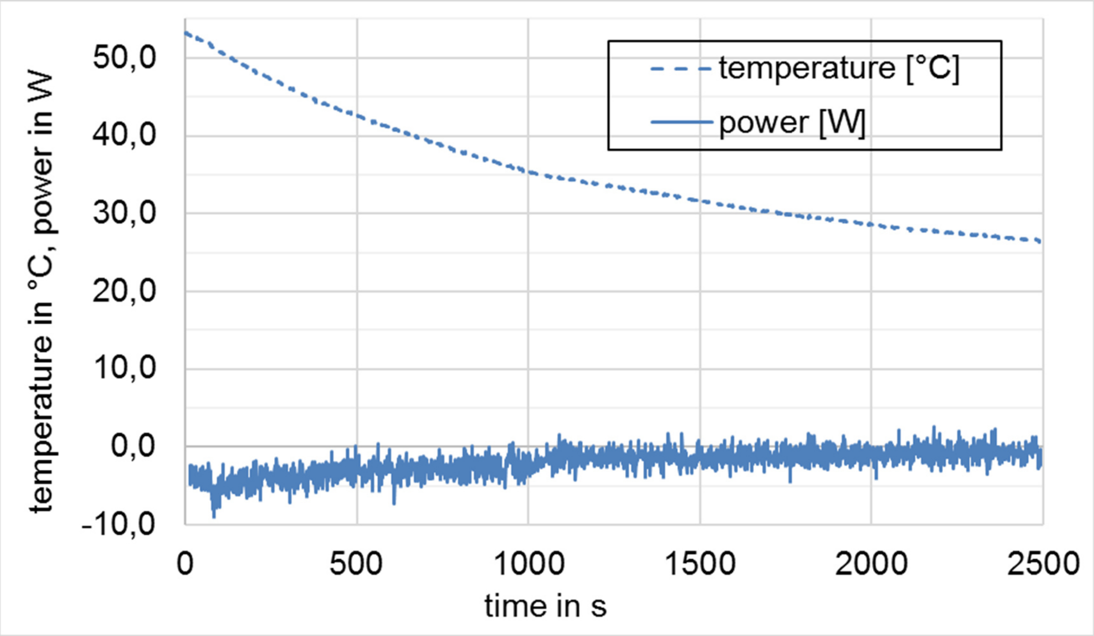

Figure 46: heat loss over reactor temperature through the reactor insulation

It can be seen that heat loss ranges between 0 and 5W even for higher temperatures (~50°C). It has to be mentioned that the initial heat loss by heat transfer between the heated reactor material (copper) and the still cold further experimental setup (e.g. sorbate reservoir) could not be quantified.

Heat loss influences all experiment results in the same way, therefore does not prohibit the comparison of experiment data.

4.8 Result overview

Table 7 gives a summary and an overview of the continuative tests conducted with the promising TCHS materials ($CaCl_2$, $MgCl_2$ and LiBr), found during the comparative tests conducted with all considered TCHS materials for this project.

Table 7: continuative test result overview

test	LiBr, water	LiBr, methanol	$MgCl_2$, water	$MgCl_2$, methanol	$CaCl_2$, water	$CaCl_2$, methanol
peak power	22W	30W	40W	45W	20W	25W
power 30s	15W	23W	24W	33W	16W	18W
energy 100s	1298J	2075J	1860J	1743J	1443J	1731J
energy 200s	2070J	3027J	2687J	2080J	2103J	2441J
total energy (300s)	2471J	3490J	3077J	2152J	2420J	2721J
mass	33,5g	33,5g	27g	27g	31,5g	31,5g
spec. power 30s	0,45W/g	0,69W/g	0,89W/g	1,22W/g	0,51W/g	0,57W/g
spec. total energy	73,8J/g	104,2J/g	114,0J/g	79,7J/g	76,8J/g	86,4J/g
Δ hydrate step	0.46 H_2O	0.48 CH_4O	0.55 H_2O	0.39 CH_4O	0.37 H_2O	0.34 CH_4O

5 Discussion

In this chapter results, findings and observations gained during the conduction of the experiments, presented in chapters 3.4 and 4, are discussed and evaluated.

5.1 Reactor design

Choosing copper as reactor material was based on the excellent thermal conductivity and corrosion resistance of copper, two properties favourable for a TCHS reactor material. The corrosion resistance of copper was put to the test by the TCHS materials in use. LiBr proved to be very corrosive against copper, but long term tests if LiBr corrosion speed decreases over time (due to passivation) were not conducted. Other tested TCHS materials showed slight forms of corrosion but with far less material loss and staining of the composite. Surface treatment of copper could pose a way to eliminate/reduce corrosion especially for the use of LiBr as TCHS material.

The reactor design (cartridge-style) was successfully tested in terms of manufacturability, ability to implement a composite into the reactor, heat release properties and leak-tightness. The prototype reactor was turned out of a solid copper cylinder, therefore the grooves for increased surface area were manufactured radially, which proved to be inconvenient during the insertion of TCHS composites into the reactor. Surface increasing grooves in axial direction would simplify the insertion of composites because composites could be inserted into each groove near the reactor flange opening and then pushed further into the reactor.

The high passive mass of the reactor proved beneficial to determine heat release and power because of ease of use and measurability, compared to heat release into a water jacket. The relative high passive mass of the reactor (500g) compared to the active mass of around 30g of TCHS material inside the reactor, led to temperature rises during hydration experiments between 0°C and around 25°C. This presents easily measurable temperature increases with standard temperature elements, enabling accurate and simple data acquisition, but keeping heat loss through the applied foam insulation around the reactor to a minimum. The high passive mass also enabled a calculation of heat release power for each TCHS composite, as described in chapter 3.5. During the use of a water/glycol jacket placed around the reactor during heat release experiments, the additional passive mass, provided by the jacket, decreased the measureable temperature increase during the experiments to a level where measurement inaccuracy started to mask possible temperature changes.

Figure 47 shows a concept to reduce the passive mass (weight) of the reactor, improve implementation/filling of composite into the reactor, reduce waste during manufacturing (compared to turning out of a solid cylinder) and reduce manufacturing time by deep-drawing, like it is used to manufacture beverage cans.

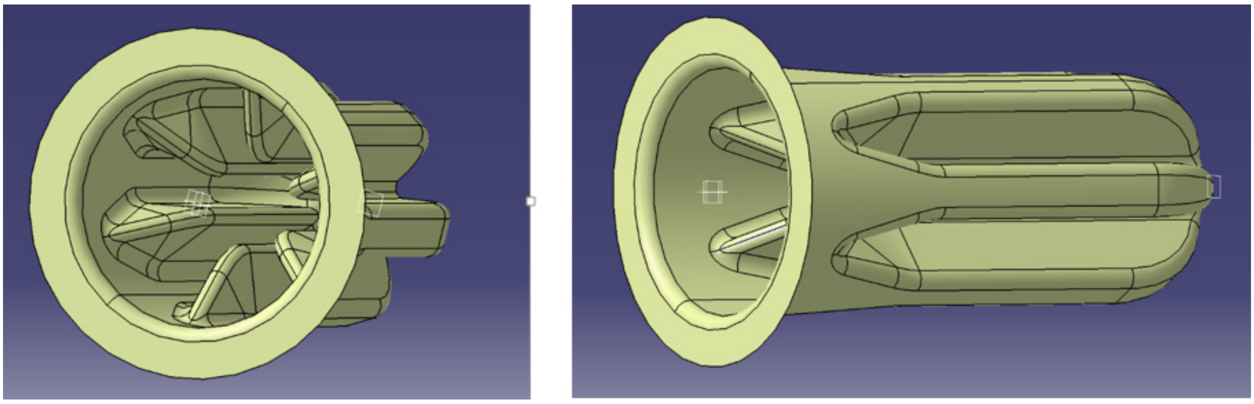

Figure 47: concept of a deep-drawn TCHS reactor cartridge [10]

5.2 Composites

The use of composites for TCHS applications proved feasible for LiBr, $MgCl_2$ and $CaCl_2$. For $MgSO_4$ and $Al_2(SO_4)_3$ the combination with a carrier material (glass wool) to form a composite was not feasible to accelerate reaction kinetics enough to achieve a sufficient heat release power, compared to LiBr, $MgCl_2$ and $CaCl_2$.

Glass wool represents a chemically inert and non-porous carrier material and therefore the theoretically possible energy density of composites is reduced compared to pure TCHS materials (e.g. $CaCl_2$) or composites with a carrier material which is reactive to the sorbate of the TCHS material itself, e.g. zeolite.

The use of a saturated aqueous TCHS material solution to impregnate/soak carrier material, poses a field for further research, regarding the use of non-saturated solutions of various compositions in order to assess a possible influence on the formation and performance of composites. Further drying temperature and time to reach maximum dehydration of a wet composite can be altered to research possible discontinuities respectively hysteresis effects during hydration and dehydration as mentioned in chapter 2.4.1 for $CaCl_2$. [22].

The use of glass wool to form a composite with TCHS materials showed a good performance on retaining TCHS materials inside the reactor and eliminate negative effects during sorption cycles, like volume increase/decrease, melting effects and structural decomposition of e.g. pure TCHS material pellets.

With the use of composites not only the advantages of base materials (carrier and TCHS materials) are integrated into the composite but also possible disadvantages of the base materials. Disadvantages like affinity for decomposition (thermal, chemical, mechanical), toxicity, price, manufacturability (automatization of composite manufacturing) and recyclability, also apply to carrier materials as well as to TCHS materials. Glass wool as carrier material does not show signs of decomposition. Glass wool as a mass production item for insulation use, indicates good availability and low price for glass wool as carrier material for TCHS composites. The availability of glass wool in different processing types (raw, roving, blankets, fleece) indicates a sophisticated automated processing capability for glass wool products by manufacturers.

Possible toxicity risks by glass wool dust and inadequate recycling possibilities (poor deposition characteristic in landfills due to low density and not thermally usable due to being non-flammable) for glass wool present drawbacks for glass wool use. Due to the water solubility of the investigated TCHS materials in this work, separation of the TCHS materials from their carrier material seems feasible by washing the TCHS material out of the carrier material in order to be able to recycle respectively dispose both materials separately and therefore more efficiently. [50]

The use of a novel filling method, with an additional TCHS material coating on the inside wall of the reactor, turned out to be preferable over various composite-only reactor fillings (glass wool, copper wool), therefore being a feasible and pursuable method for further research. The idea for this combination was derived from the demand for high heat release power, rather than heat storage density, for the intended application in motor vehicles. Pure TCHS-material-coating sticking to the reactor walls is intended to provide better thermal conductivity, to conduct heat into the reactor material, but be thin enough to have a sufficient sorbate transfer. Composite (glass wool + TCHS material) was utilised to maximise TCHS material mass inside the reactor to achieve not only initial heat release power but also a sufficient energy storage quantity.

Formation of TCHS composites with copper wool was not effective, because the available copper wool proved to repel the aqueous TCHS material solution and therefore solution had to be forced into the copper wool by injecting it with a syringe. This led to a composite consistence resembling a solid TCHS material with embedded copper wool fibres than copper wool with adhered TCHS material. The copper wool in use consisted of relative

thick fibres, using copper wool with thinner fibres and/or a surface treatment before composite preparation could pose a solution to create a sufficient composite with copper wool as carrier material.
The use of glass wool could eradicate previous issues (melting and volume change) related with the use of pure TCHS material in TCHS reactors but turned out to be not feasible in order to increase reaction kinetics of $MgSO_4$ and $Al_2(SO_4)_3$.

5.3 Sorbate

Two sorbates were used to conduct TCHS experiments, water and methanol. Both sorbates showed good sorption kinetics with $MgCl_2$, $CaCl_2$ and LiBr with an advantage for methanol in terms of better peak heat release power and total heat release. In terms of desorption characteristic of both sorbates, methanol far exceeded water regarding desorption speed and minimum desorption temperature, to obtain complete desorption after a sorption experiment. Reason for the superior behaviour of methanol compared to water, is believed to be caused by the higher vapour pressure of methanol, lower heat of evaporation and lower heat capacity compared to water. It is stated that these properties lead to more gaseous sorbate present for the TCHS material to absorb, especially for low temperature applications, where vapour pressure of water becomes inadequate for sufficient reaction kinetics. The superior desorption performance of methanol compared to water as sorbate, could be due to lower binding forces of methanol. Methanol has a dipole moment of 1.7 D (Debye) compared to 1.85 D for water. The stronger dipole moment of water leads to stronger van der Waals-type binding forces between absorbed water and the TCHS material, leading to higher temperatures for the desorption to start, respectively a slower desorption speed. Lower heat of evaporation and heat capacity for methanol than for water can also contribute to better desorption performance, because of less heat required in order to overcome heat of evaporation and reach the temperature level needed in order to achieve desorption. [51], [52]

Methanol as sorbate posed safety concerns because of its flammability and toxic character. A further safety relevant property of methanol to be considered during use is its practically invisible flame during combustion, complicating firefighting if necessary. Carbon monoxide and formaldehyde can be formed during methanol combustion under oxygen deficit. [53], [49]

5.4 $CaCl_2$

Based on findings of a previous research [13], $CaCl_2$ was in use to establish a performance base line for the reactor used in this work. Different composites based on $CaCl_2$ as TCHS material were tested and evaluated. The best result was achieved by combining a thin coating of pure $CaCl_2$ on the inside of the reactor in combination with a composite of $CaCl_2$ impregnated glass wool.

$CaCl_2$ showed fast reaction kinetic with both tested sorbates, water and methanol. Methanol outperforming water slightly in terms of peak power, temperature increase, total heat release and desorption performance.

$CaCl_2$ showed a low sorbate uptake resulting in a hydration step of around 0.4 molecules of sorbate by one molecule $CaCl_2$ for both sorbates, water and methanol. Theoretically possible sorbate uptake should be in the range of a hydration step of 6 molecules of sorbate per molecule of salt, on the basis of data presented in chapter 2.4.1. Cause for the experienced low hydration steps during experiments with $CaCl_2$, is assumed to be the low vapour pressure of both sorbates, for temperature levels around 20°C. The sorption time difference between continuative tests (5 min, hydration step of 0.4) and comparative TCHS material tests (60 min, hydration step of 1.5), can explain why a hydration-step-difference of around 1.1 was observed between both tests. Further improvements in terms of vapour transfer into and heat transfer out of the composite could help to improve sorbate uptake speed. $CaCl_2$ showed increased sorbate uptake for both sorbates (water and methanol) during lower reactor and therefore plausibly also lower composite temperatures. The increased sorbate uptake can be explained by a sorbate uptake inhibiting influence of higher temperatures, which would correspond with the ability of $CaCl_2$ to be desorbed after desorption temperature is reached.

Copper showed marginal signs of corrosion/oxidation during the use with $CaCl_2$-composites, making it a preferable combination because of the heat release properties of $CaCl_2$ and the characteristics of copper regarding thermal conductivity and corrosion resistance against $CaCl_2$. [54]

Processability of $CaCl_2$ to form a composite with glass wool was affected by the high affinity of glass wool to soak aqueous solution of $CaCl_2$ (as well as aqueous solutions of the other tested TCHS materials) and therefore measures beyond draining (with the use of gravity) had to be taken in order to remove excess $CaCl_2$ solution from the composite.

Excess solution was drained using a sieve (Büchner-funnel) in combination with a vacuum pump.

For a wide industrial application of $CaCl_2$, the availability of $CaCl_2$ is a crucial point. $CaCO_3$ as a base material for $CaCl_2$ production takes up more than 4% of the earth's crust and can be found throughout the world as limestone. In addition to that, $CaCl_2$ is currently an essential raw material for agricultural fertilizers and livestock nutrition additives, with an annual supply in excess of 3.6 million tonnes for 2015, making it readily available and cost effective with 36 €/kg purchased via *Sigma Aldrich*. [55], [56]

Safety concerns are limited to eye irritation and general chemical spill prevention measures. Recycling of $CaCl_2$ is dependent on the long-term stability of $CaCl_2$ under TCHS use and therefore, if $CaCl_2$ can be reused or if it is poisoned by unwanted chemical reactions.

5.5 $MgSO_4$

Figure 10 assigns $MgSO_4$ with the highest energy density of all examined TCHS materials in this work with a stated reaction temperature around 220°C. High energy density marks a favourable attribute for a storage material and therefore $MgSO_4$ was included as TCHS material for experiments. In order to achieve anhydrous $MgSO_4$ a high temperature (270°C) is needed, which is too high to achieve with the temperature levels provided by hot engine coolant or oil, but $MgSO_4$ shows significant desorption capability far below the temperature needed to reach the anhydrous state. Despite its high energy density and the use of a carrier material to form a composite, possibly able to enhance reaction kinetics, $MgSO_4$ only shows slow reaction kinetics during sorption and therefore the achievable peak power was low. Therefore, $MgSO_4$ was not considered feasible to develop a TCHS device with the focus on short reaction times and high power.

5.6 $Al_2(SO_4)_3$

$Al_2(SO_4)_3$ poses the second TCHS material from the group of sulphate compounds. Like $MgSO_4$, $Al_2(SO_4)_3$ has a high energy density and the ability to nearly become anhydrous with dehydration temperatures of around 155°C as shown in chapter 2.4.3. Unfortunately, as indicated by slow sorption speeds during experiments conducted by other researchers, the use of glass wool to form a composite with $Al_2(SO_4)_3$ could not improve sorption kinetics, in order to achieve sufficient peak heat release power during heat release experiments. [29]

Both sulphate TCHS materials examined ($MgSO_4$ and $Al_2(SO_4)_3$) have shown a slow sorption kinetic and high possible energy density. The slow sorption kinetic of both sulphate TCHS materials makes the use as TCHS materials for cold start improvement applications for motor vehicles unfeasible, because fast heat release and short reaction times are necessary for this application. Due to their high possible energy density, both materials could be more feasible for heating applications where a slower reaction time and a lower peak heat release power can be tolerated, like for example heating applications for buildings.

5.7 LiBr

LiBr provided good sorption characteristics both with water and methanol as sorbate. Compared to $CaCl_2$, LiBr achieved slightly better performances in terms of total heat release and peak power with both sorbates. Similar to $CaCl_2$, LiBr showed only a small sorbate uptake of roughly 0.5 (water for and methanol) parts sorbate per part LiBr during continuative tests (5 min sorption time). Due to the characteristic of LiBr to form only a 2-hydrate at temperatures above 20°C, the achieved sorption steps of LiBr with 5 min sorption time are, in relation to the theoretically achievable hydrate steps, higher than the relative sorption steps achieved by $CaCl_2$. This indicates a higher utilization of the total sorption potential of LiBr than for $CaCl_2$. $CaCl_2$ could have more potential to increase performance than LiBr, due to more utilisable sorption potential left.

Significant drawback of LiBr was the strong corrosive character against the reactor material (copper). Findings by other researchers confirm corrosive properties of LiBr against copper and state that with higher temperatures (ranging from 20°C to 110°C) and higher LiBr concentration (400g/L and 700g/L aqueous solution) corrosiveness increases. [57]
Corrosion products are assumed to be a mixture of CuBr and $CuO/Cu(OH)_2$ with a crystalline/granular morphology, for corrosion experiments with 400g/L LiBr aqueous solution. For experiments with 700g/L LiBr solution, a gelatinous and amorphous morphology of the corrosion products was found, believed to consist of CuBr and $CuBr_2*3Cu(OH)_2$. [57]

A possibility to prevent corrosion of copper under the influence of LiBr presents the use of inhibitors, that form a passive layer on the metal's surface, that protects the underlying metal from further corrosion. The passive layer consists in most cases of insoluble salt which was formed by the inhibitor and the ions of the corroding metal. Further copper-nickel alloys were examined with positive results in terms of reduced localised corrosion but behaved like pure copper in terms of general corrosion. The combination of nickel containing copper alloys and inhibitors can lead to susceptibility for pitting corrosion, with the exception of molybdate and tetraborate anions to inhibit Cu70/Ni30 alloy from pitting. [58]

Better performance in terms of total heat release, peak power and desorption characteristic with methanol as sorbate corresponds with the findings for $CaCl_2$ and is believed to be due to differences between water and methanol in terms of vapour pressure and dipole moment as described in chapter 5.3.

LiBr was the most expensive TCHS material investigated with a cost of 165 €/kg purchased by *Sigma Aldrich*. Literature states, that a sufficient lithium supply for the next 100 years is possible, including lithium demand growth by increased battery production. Concerns were raised regarding challenges of lithium deposit mining development, for example financial feasibility and political stability because of the high concentration of 70% of the worlds lithium-brine resources in South-America and China. [59]

Of all examined TCHS materials in this work, LiBr can be considered as the most dangerous material regarding several risk and safety statements including acute oral toxicity and the possibility of dangerous gases under exposure to fire. This implies the need for possibly higher measures of safety in order to use LiBr, than for less toxic/dangerous TCHS materials, for mass-produced TCHS devices.

Recyclability of LiBr at the end of a TCHS device life-cycle would rely on the chemical stability of LiBr during service life and therefore, if the TCHS material has not reacted with e.g. the reactor material or oxygen. LiBr recycling could be carried out by dissolving LiBr in water and separating the aqueous LiBr solution from the insoluble carrier material.

5.8 $MgCl_2$

$MgCl_2$ proved to be the most effective of the TCHS materials tested, in terms of peak heat release power, based on the continuative test regime. $MgCl_2$, like $CaCl_2$ and LiBr, performed better with methanol as sorbate for sorption and desorption, than with the use of water as sorbate. Cause of this behaviour is believed to be the same as for $CaCl_2$ and LiBr (chapters 5.4 and 5.7), differences between water and methanol regarding the properties vapour pressure and dipole moment. This allows for methanol to provide fast absorption and good desorption (chapter 5.3), compared to good absorption but weak desorption characteristics for water used as sorbate. Despite the good desorption characteristic of methanol used as sorbate, $MgCl_2$ shows a different desorption characteristic than $CaCl_2$ and LiBr. $MgCl_2$ could not be fully desorbed during 30 min at 110°C desorption temperature after the first two sorption runs with methanol, leaving residual methanol in the composite. Decreasing methanol uptake of not fully desorbed composite led to an operation point of the composite, where sorption and desorption rates under the given conditions were equivalent. This means, if the desorption rate of the $MgCl_2$ composite could be increased respectively a longer desorption time could be feasible in an intended working environment for a TCHS device, the balance point of $MgCl_2$ sorption and desorption could be shifted to higher peak heat release power levels of around 65 W.

Like $CaCl_2$ and LiBr, $MgCl_2$ could only achieve a sorbate uptake of 0.55 (water) and 0.39 (methanol) parts of sorbate per part $MgCl_2$ during continuative tests. Taking into account the dehydration curve of $MgCl_2$ shown in chapter 2.4.5, the maximum possible hydration step for $MgCl_2$ could be between 4 (110°C) and 5 (150°C) depending on the dehydration temperature. Therefore, $MgCl_2$, similar to $CaCl_2$ and LiBr, shows potential for improvements in terms of heat release, when the reaction kinetic could be improved.

The $MgCl_2$ composite showed marginal reaction with the reactor material (copper), but no long-term tests were conducted. The use of an evacuated system as intended in this work would prevent copper corrosion under the influence of $MgCl_2$, by eliminating oxygen which presents an important reactant for copper corrosion. [60]

Considered to be a non-dangerous and non-toxic material, $MgCl_2$ poses a favourable TCHS material for the use in motor vehicles with their higher proneness for accidents than stationary applications.

Base materials for $MgCl_2$ production vary from natural brines, seawater, minerals like carnallite and dolomite and by-products respectively waste products of other industrial processes, like titanium production via the *Kroll*-process. In general, it can be stated that a majority of magnesium processing is done in China, which poses a dependence on a big player in terms of price and availability. In contrast, magnesium resources as base materials for magnesium compounds like $MgCl_2$ are considered virtually unlimited by the U.S. Geological Survey and globally widespread. [40], [61], [62], [63]

5.9 Summary

During comparative testing, it showed that $Al_2(SO_4)_3$ and $MgSO_4$, despite having a high theoretical energy density, reaction kinetics for both materials proved too slow for an application as TCHS material for use in motor vehicles.

From the three remaining TCHS materials, which displayed good sorption performance during comparative testing, $MgCl_2$ presented the best heat release power but had disadvantages compared to LiBr and $CaCl_2$ concerning the desorption characteristic when methanol was used as sorbate. Main disadvantage of LiBr is its strong corrosiveness against copper which has to be addressed and its high price compared to $CaCl_2$ and $MgCl_2$. $CaCl_2$ showed lower peak heat release power than $MgCl_2$ but its desorption characteristic was better than the desorption characteristic of $MgCl_2$, when methanol was used as sorbate for both materials.

Therefore, $MgCl_2$ and $CaCl_2$ were considered the most feasible TCHS materials, out of the five materials tested, for TCHS devices intended to be utilized in motor vehicles.

6 Error analysis

6.1 Systematic Errors

Temperature measurements were taken by thermocouples “Type K” combined with the on-board input settings for “Type K” thermocouples provided by *LabVIEW* software. The use of 5 thermocouples to measure the temperature at different places of the reactor with very consistent and congruent temperature curves ensured adequate measuring accuracy, even considering the relatively wide inaccuracy range of “Type K” thermocouples of ±2.2°C or ±0.75%.

Linearization was utilised to calibrate both pressure sensors. Plausibility of the pressure sensor data was checked regularly by comparing the pressure data with the data provided by vapour pressure charts for the sorbate (water or methanol) for the present temperature.

6.2 Operating and Evaluation Errors

Manual composite preparation and implementation into the reactor posed an error source because of inevitable slight differences that occur with manual work, as standardized the procedure might be.
Due to frequent alterations to the test bench and to the reactor (setup changes to perform sorption as well as desorption) slight changes in terms of thermocouple position and contact to the reactor wall had to be accepted.
Providing a leak free TCHS system and consistent low system pressures were monitored by two installed pressure sensors.

To evaluate the performance of different TCHS materials, calculations based on measured reactor temperatures were conducted. Heat loss through the reactor insulation was not taken into account for those calculations. Figure 46 gives a relation between the reactor temperature and the power of heat loss through the reactor insulation. Figure 46 shows only marginal heat loss through the insulation, which occurs for all conducted experiments and therefore does not hinder comparability of the experiment data.

6.3 Simplification

Differences between the utilised experiment setup and the pursued finished product of a mass produced TCHS device for motor vehicles have to be considered. The major difference of the prototype compared to the possible future final product, is assumed to be because of manufacturing restrictions experienced during the creation of the cartridge-type prototype reactor. This manufacturing restrictions in terms of limitation to basic workshop tools including a lathe, led to a high passive mass and relative small heat exchange area, compared to other prototype TCHS reactors [13]. Additionally, the norm parts used to construct the periphery of the TCHS reactor (e.g. sorbate tank, valves and connectors) provided additional passive mass that has to be considered while comparing the experiment results with other studies. For the comparison of different TCHS materials, the high passive mass posed little problem because of the consistent experimental environment for all tested TCHS materials.

6.4 Relevant Errors

Due to the fact that the goal of this work was to compare different TCHS materials, it is most important to test all materials under the same circumstances.

Effects of systematic errors were reduced by multiple sensors for temperature and pressure as well as multiple reruns of the same experiment.

Operational errors were minimized by standardization (composite preparation) and monitoring of the sensor signals (pressure and temperature).

Simplifications of the reactor design and the experimental setup were equal for all conducted experiments and are considered to be feasible to allow for appropriate evaluation of the tested TCHS materials.

7 Summary and Outlook

7.1 Summary

Based on the data and knowledge gained during the preparation of this work, it can be stated that the application of a cartridge style TCHS reactor was successful, considering the early prototype stage of the reactor design, by minimizing leakage potential, simplifying heat transport and promoting modularity of TCHS systems.

Despite high theoretical energy densities, not all tested TCHS materials proved to be feasible for the working conditions defined for TCHS devices, intended to be implemented into motor vehicles. The demand for high power-density for this application could only be achieved by $CaCl_2$, $MgCl_2$ and LiBr. $MgSO_4$ and $Al_2(SO_4)_3$ did not prove feasible to gain enough heat-release power, even when combined with a carrier material to form a composite. Therefore, $MgSO_4$ and $Al_2(SO_4)_3$ are not feasible for the intended working environment, cold start and warmup phase improvement for motor vehicles.

The use of different sorbates (water and methanol) proved, that methanol seems to be the better sorbate, with better peak heat-release power during sorption experiments and superior desorption characteristics compared to water. Further, the low freezing temperature of methanol would enable the use of TCHS devices below a temperature of 0°C, without the addition of antifreeze, as it would be necessary with water as sorbate.

TCHS shows great potential for energy storage but its early development stage, compared to latent or phase change heat storage and other energy storage solutions, like e.g. electricity storage with battery technology, does not promote commercial use.

7.2 Improvements and Outlook

This chapter focusses on lessons learned from the conducted experiments and the derivation of improvements for further research activities, based on the findings of this work.

As mentioned in chapter 5.1, the high passive mass of the reactor was beneficial for ease of TCHS-material comparison, but would be detrimental in order to achieve high heating rates for the material outside of the reactor (e.g. engine oil or coolant). Therefore, further efforts have to be taken to manufacture a reactor with lower passive mass and higher contact area between TCHS composites and the reactor.

During the preparation of TCHS composites, a saturated aqueous solution of TCHS material was used to soak carrier materials. The aqueous solution had almost a vegetable oil like consistency, that sticks very well to glass wool, creating a need to remove excess solution from the carrier material, before inserting the wet composite into the reactor. A parameter variation in terms of saturation level of the aqueous TCHS-material solution utilised to soak carrier material could be conducted, in order to optimise accumulation of TCHS material on the carrier material (glass wool).

Further the effect of different heating rates and times in order to achieve initial dehydration of the composite, poses a field for continuative research, in order to find and characterise possible hysteresis effects during sorption and desorption cycles. The knowledge, how those effects influence overall performance of TCHS composites, can help to improve the performance of TCHS. An example for hysteresis was described in chapter 2.4.1 for $CaCl_2$.

Development of an automated respectively mechanical composite preparation method respectively reactor filling method to further standardise the experiment preparation would be beneficial. The primary obstacle for an automated insertion of composite into the prototype cartridge-style reactor, were radial fins inside the reactor for increased heat exchange area. Axial fins inside the reactor could provide enough clearance for e.g. preformed composite blocks to be inserted into the reactor, reducing the influence of filling the reactor by hand on the performance of composites.

In order to achieve the goal to establish TCHS as a viable technology to fight climate change by reducing GHG emissions, improvements in terms of TCHS-material performance have to be made, as well as improvements in reactor design and manufacturability. Modern respectively novel manufacturing processes like 3D printing could help to achieve those improvements, for both TCHS material and reactor development.

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