



Development of a Prototype Latent Heat Thermal Energy Storage System

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Going to press

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I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume. If text passages from sources are used literally, they are marked as such. I confirm that this work is original and has not been submitted elsewhere for any examination, nor is it currently under consideration for a thesis elsewhere.

Vienna, October 2019

Abstract

Thermal energy storage systems can balance volatile production and consumption of heat at different temperature levels and time scales. The temperature target level is medium to high, focusing on storage temperatures up to 350 °C with potential applications in solar thermal energy production, or industrial processes. Utilizing phase change materials as storage material, the energy density can be higher compared to other storage systems. Because of the low thermal conductivity of many phase change materials in the solid state, heat transfer is highly transient. Enhancing the heat transfer ability is key to improving this storage technology; but heat transfer mechanisms and melting phenomena are also worth studying, especially when looking at industrial scale prototypes and the improvement of this level of technology.

This work aims to address the topic of heat transfer enhancement and attaching aluminum fins to a steel tube. For this purpose, a new fin design and a novel attachment method are developed. Two test rigs in lab-scale are built and performance measurements of such a storage units are executed. In this this test rigs, sodium nitrate is used as an affordable, non-toxic and highly promising phase change material (PCM). The melting temperature is in the range of with life steam temperatures in solar thermal power plants. The test-rigs are equipped with a single aluminum finned steel tube filled with heat transfer fluid. The storage vessel is a cylindrical tank with a finned tube heat exchanger. The volume between the tubes and the shell is filled with PCM. Thermal oil is used as a heat transfer fluid. The temperatures and mass flows are processed in a process control system and analyzed later on.

The experiments provide detailed data of the melting front development in the storage units. By employing multiple temperature testing points, energy balance and other performance indicators are provided for the two different fin geometries. The heat transfer from the heat transfer fluid into the storage material is described in detail and quantified. In addition, a new attachment method for aluminum fins is presented.

With the novel fin geometry, melting performance is improved significantly. The heat transfer coefficient allows storage power prediction for future storage systems. And the highly promising manufacturing method for bimetallic finned tubes enables hexagonal cross sections and large-scale production. With this contribution to the development of latent heat thermal energy storage systems, energy systems will become more efficient. Industrial scale application of this storage type will help to reduce primary energy inputs through reduction of fossil fuel needs which will be one of the most threatening global challenges in the coming decades.

Kurzfassung

Thermische Energiespeicher können fluktuierende thermische Verbraucher und Produzenten in unterschiedlichen zeitlichen Dimensionen und Temperaturniveaus sinnvoll koppeln. Dadurch können höhere Nutzungsgrade der eingesetzten Primärenergie erreicht werden. Dabei steht der Temperaturbereich bis 350 °C im Fokus, welcher etwa für solarthermischen Kraftwerke oder industrielle Prozesse gut einsetzbar ist. Das Speicherkonzept des Latentwärmespeichers mit dem Einsatz von Phasenwechselmaterialien als Speichermaterial ermöglicht hohe Energiedichtungen und dadurch geringere Speichervolumen. Ein häufiger Nachteil bei Phasenwechselmaterialien liegt in der schlechten Wärmeleitung im festen Zustand und im transienten Wärmeübertragungsverhalten.

Im Rahmen dieser Arbeit wurden Latentwärmespeicher Prototypen im Labormaßstab entwickelt und experimentelle Untersuchungen durchgeführt. Der Wärmetransport wird mit Hilfe von Aluminiumrippen die auf einem Stahlrohr fixiert werden, erhöht. Als Speichermedium wird leicht verfügbares, konstengünstiges und ungiftiges Natriumnitrat verwendet. Der Schmelzpunktes ist passend für Anwendungen im Hochtemperatur-Solarthermiebereich und Schmelzenthalpie ist relativ groß. Das Wärmetauscherrohr wird vertikal in einem zylinderförmigen Speicherbehälter platziert. Das Stahlrohr wird vom Wärmeträgermedium durchströmt; das Phasenwechselmaterial ist zwischen den Rippen und dem Speicherbehälter angeordnet. Temperaturen und Massenströme können über ein Prozessleitsystem geregelt und für eine spätere Auswertung aufgezeichnet werden.

Insgesamt wurde zwei Versuchsstände konstruiert und gebaut die sich vor allem durch ihre Rippengeometrie unterscheiden. Auf Basis der Messungen kann die Entwicklung der Schmelzfront rekonstruiert werden. Außerdem wird die Energiebilanz für den Speicher aufgestellt und die wesentlichen Kenndaten wie Leistung, Kapazität aber vor allem das dynamische Verhalten gemessen. Auch der Wärmeübergang vom Wärmeträgermedium in das Speichermaterial wird genau beschrieben. Durch die Optimierung der Rippengeometrie konnte das Aufschmelzverhalten verbessert werden. Außerdem wurde eine neue Methode zur Befestigung von Aluminiumrippen auf einem Stahlrohr entwickelt. Mit ihrer Hilfe lassen sich auch sechseckige Querschnitte von Aluminium-Stahl Verbundrippenrohren produzieren, die sich dadurch effizient in einem Latentwärmespeicher anordnen lassen.

Im Rahmen dieser Dissertation wurde die Technologie für Latentwärmespeicher und Rippenrohre weiter entwickelt um sie effizienter und besser zu machen. Latentwärmespeicher können den Energieverbrauch reduzieren und den Nutzungsgrad von Wärme wesentlich erhöhen. Im Hinblick auf die kommenden Jahrzehnte ist es notwendig, jede verfügbare Maßnahme zur Verringerung der Emissionen und zum effizienteren Energieeinsatz zu ergreifen, dabei kann der Latentwärmespeicher eine wichtige Rolle spielen.

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This thesis summarizes the work in the field of thermal energy storage with phase change materials at the Institute of Energy Systems and Thermodynamics at TU Wien in the past six years. Most of the work was done within two nationally funded research projects GreenStorageGrid (#836636) and BiMeRi (#843934). I would like to express my appreciation to the financers of those projects. Furthermore, my employment as a university assistant at TU Wien for the past five years enabled the completion of this thesis, and it also provided many other interesting experiences such as teaching.

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Nomenclature

Acronyms

CFD	computational fluid dynamics
CSP	concentrated solar power
DLR	German Aerospace Center (DLR)
DSC	differential scanning calorimetry
DSG	direct steam generation
HDPE	high density polyethylen
HFM	hot flow meter
HTF	heat transfer fluid
IB	implementation barrier
IET	Institute of Energy Systems and Thermodynamic at TU Wien
IR	infrared radiation
LCOE	levelized costs of electricity
LFA	laser flash apparatus
LoU	level of utilization
ORC	organic rankine cycle
PA	polyamids
PCM	phase change material
PCS	process control system
PDE	partial differential equation
PV	photo voltaic
PV	photovoltaic
SL-PCM	solid-liquid phase change material
\mathbf{SM}	storage material
SS-PCM	solid-solid phase change material
TES	thermal energy storage
TGA	thermogravimetry
THB	transient hot bridge

Greek symbols

β	heating rate	$ m Kmin^{-1}$
ΔH_r	Reaction enthalpy	$\rm Jmol^{-1}$
ϵ	dimensionless fin factor	_
η	dimensionless number used in derivations as a substitution	_

γ	liquid fraction
λ	heat conductivity
ρ	density

Subscripts

b	boundary
char	charging
dis	discharging
e	extrapolated
f	final
i	initial
1	liquid
loss	losses
lrv	lower range value
melt	melting point
pk	peak
s	solid
sen	sensible
urv	upper range value

Roman symbols

a	thermal diffusivity	$\mathrm{m}^2\mathrm{s}^{-1}$
c	costs	€/kWh
c_p^*	equivalent specific heat capacity	${ m kJkg^{-1}K^{-1}}$
c_p	specific isobaric heat capacity	${ m kJkg^{-1}K^{-1}}$
$c_{p,app}$	apparent specific heat capacity	${ m kJkg^{-1}K^{-1}}$
E	energy	kW h
f	heat flux	${ m Wm^{-2}}$
k	heat transfer coefficient	${ m W}{ m m}^{-2}{ m K}^{-1}$
k_N	dimensionless number in solution of Neumann's problems	_
L	latent heat of fusion	$ m kJkg^{-1}K$
m	mass	kg
P	power	kW
St	Stefan number	_
T	temperature	$^{\circ}\mathrm{C}$
t	time	S
U	voltage	mV
w	energy density	${ m kW}{ m h}{ m m}^{-3}$
X	solidification front position	m
x	distance	m



1. Introduction

The increasing worldwide demand for energy, combined with the widespread use of fossil fuel resources and the global warming effect of their ensuing emissions, lead to some very crucial questions for the coming decades. How can this energy demand be satisfied by renewable energies? How can this energy demand be reduced and the application be made more effective? What will be the sources of energy utilized in our future energy systems? How can all of this be considered alongside reducing the global inequity in energy consumption? Based on these huge questions, technological development can provide solutions for some aspects.

1.1. Energy Transition and Global Warming

At the moment, human activities have caused a global warming of 1 °C above the preindustrial level. The global mean surface temperature will likely reach 1.5 °C between 2030 and 2052, according to the Global Warming of 1.5 °C report from the Intergovernmental Panel on Climate Change [46]. This warming distribution is not homogeneous; land regions are affected more than oceans. The accumulated anthropogenic emissions will persist for centuries to millennia and will cause long term changes in the climate system, but these emissions alone will not cause a global warming of 1.5 °C. Reaching and sustaining net zero global anthropogenic CO₂ emissions would halt global warming on a multi-decadal time scale and this is good news, but it requires a CO₂ emission reduction down to zero in the next few years in order to reach net zero between 2040 and 2055.

The main impact of global warming on biodiversity and on ecosystems is the loss of climatically determined geographic ranges for many species. With less warming this loss will be minimized and, therefore, the impact on biodiversity and the ecosystems will also be minimized. In addition, global warming affects the oceans; rising ocean temperatures increase ocean acidity and decrease ocean oxygen levels. Marine diversity, fisheries and ecosystems, and their functions and services to humans will be less affected when warming is limited. Probably the highest climate-related risks, as mentioned in the report, are: health, livelihoods, food security, water supply, human security, and economic growth. To accentuate this, heat-related morbidity and mortality will increase, and a net reduction in yields of maize, rice, wheat and other crops will also occur. Summing up, the need for adaptions will decrease with lower global warming.

In order to reach this ambitious target, the International Renewable Energy Agency (IRENA) has provided a report on how to reach climate sustainability [47]. The report clearly states that the nationally defined climate-related policies are not ambitious

1. Introduction

enough to meet the target. Three pillars are mentioned for closing the sustainability gap:

- increasing share of renewables
- reducing global energy demand
- increasing electrification pathway for end-use sector

The share of renewable energy in the total primary energy supply in 2016 has to increase from 14% to 65% in 2050 which corresponds to a gain of 350 EJ. The primary energy supply can be split into the power, industry, transport, and building sectors. The power production sector needs to be almost completely de-carbonized by 2050. This can be achieved with using renewable energy sources, energy efficiency, and flexible power systems. Annual additions of renewable power capacity are mentioned with 600 GW globally. In order to reach this growth, all types of renewable energy have to be utilized and investment into renewables has to increase drastically so that the share of decentralized renewable power will increase significantly. The situation is worse for the other sectors. Industry's energy demand is provided by only 14% renewables, transport has a 3% share in renewables, while the building sector has one third. The IRENA report draws a clear picture of the present situation and the course of action required for the realization of global warming reduction targets. Hence, concrete actions like policy, regulations, and financial innovation are promoted.

The total primary energy supply in Austria is based on non-renewable energies. Coal, gas, and oil count for two thirds of the primary energy demand, based on the statistics [11]. For power production the share is reversed; two thirds is renewable power production mainly from water power plants. From a global perspective, the industry, building, and transport sectors count for the majority of the CO_2 emissions. Hence, these sectors can contribute most to reducing dependence on fossil fuels, and bring Austria on track to contributing to the climate targets.

From a technological perspective, the IRENA Renewable Power Generation Costs report [48] points to the direction of the technological development. Solar and wind will be the backbone of renewable power source. The main part of solar production will come from photovoltaic (PV), but an increasing share will also come from concentrated solar power (CSP) plants. Prices for PV and CSP will soon reach the fossil fuel range. While photovoltaic has dropped down to 0.10 USD/kWh in 2017, CSP has reached 0.22 USD/kWh. In any case, a global change in energy systems involves handling volatile energy production and consumption, as well as higher decentralized conversion. For this purpose, energy storage systems will play a key role in future energy systems. Electrical storage systems and thermal storage systems can increase the level of utilization of renewable energy systems significantly. Almost all commissioned CSP plants in the past three years are built with thermal storage systems. Volatile high temperature waste heat from the cement and steel industry e.g. has high potential for further utilization with thermal storage systems. They provide the ability of load shifting and can supply other processes (electricity production, heat supply, etc.) with a continuous and controlled amount of heat. Storage, electrical and thermal, can contribute in the mentioned way to an efficient utilization of energy for present and future generations.

1.2. Thermal Energy Storage Systems

A variety of thermal energy storage (TES) systems exist for different applications and temperature levels. Different storage methods for individual applications are available at diverse technology readiness levels. A good introduction and overview of the topic is provided by the book of Dincer and Rosen in [21] or by Frazzica and Cabeza in [29] and Cabeza and Tay in [14]. Energy storage devices in general and TES in particular are applied for the following reasons:

- reducing energy effort / increasing level of energy utilization
- reducing energy costs
- increasing the flexibility of operation
- reducing capital and operational expenditure
- reducing equipment size
- reducing emission and fossil fuel input

The advantage of TES systems are manifold. One of the most common applications may be the household electric hot water tank. Compared to a flow-type, on demand heater, the maximum installed heating power is reduced drastically. This may result in a lower connection power to the power grid and lower electricity costs for the consumer. In addition, the availability of hot water increases as discharging of the storage is possible for two or more consumers at the same time. In the specific case of cheaper electricity during night-time hours, energy costs can be reduced when the storage capacity exceeds the one day hot water demand and is charged during the night. Storage systems can smooth peaks enabling a reduction in the size of the heater, independently of the used heating system. Finally, emissions may be reduced through effective energy utilization. Depending on the heater's energy source, fossil fuel input can be decreased compared to systems without storage.

In thermal energy storage systems, energy is transferred to and from the storage in the form of heat. Other energy storage systems comprise of mechanical, chemical, biological and magnetic storage systems as listened in [21]. Mechanical storage systems like flying wheels, pumped hydro, or compressed air will not be addressed within this work. Chemical storage systems like electrochemical batteries are also not focused on here.

1.2.1. Storage Parameters and Characterization

Comparing different TES systems can be done with the help of technical, environmental, economical, and other criteria. Due to the huge variety of TES methods and applications, comparisons often become complex, especially when including energy storage in general (batteries, pumped-hydro, etc.) into the analysis. Some of the criteria are discussed here, for the others, refer to the book from Dincer and Rosen [21]. In Table 1.1 some of the main parameters describing a TES system are presented.

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Parameter	Description	Unit
E	Capacity	kW h
P	Power rate	kW
t_{char}	Charging time	h
t_{dis}	Discharging time	h
η_B	Exergetic efficiency	-
m	Mass of storage material	$_{ m kg}$
T_i	Lower storage temperature	$^{\circ}\mathrm{C}$
T_{f}	Upper storage temperature	$^{\circ}\mathrm{C}$
P_{loss}	Losses to the surrounding	kW
w	Energy density	${ m kW}{ m h}{ m m}^{-3}$
LoU	Level of utilization	%
\mathbf{SM}	Type of storage material	-
HTF	Heat transfer fluid type	-
c	Costs	€/kWh

Table 1.1.: TES technical parameter

Capacity E One of the main values is the storage capacity, or the amount of energy which can be stored. Depending on the energy storage type, the capacity can reach from a few Wh, like a battery, to GWh for pumped hydro storage systems. The large TES systems, i.e. the storage for the Cerro Dominador CSP plant in Chile, can provide 110 MW of power for 17.5 h. Regarding the cumulative installed energy storage capacity, the global energy storage database [110] provides data for many energy storage projects worldwide. According to the database, the largest energy storage capacity is provided by pumped hydro. A fraction amount of that capacity represents electrochemical and thermal energy storage. The TES fraction has increased with the addition of new CSP plants in the past 15 years as mentioned in the IRENA report [48], but also the electrochemical storage capacity has also increased with the development of new batteries. For TES, a main factor for capacity is the temperature interval in which the storage is operated, limited by the lower and upper storage temperatures. For sensible TES systems with constant specific heat capacities, doubling this interval leads to double capacity. For latent heat and thermochemical TES, the sensible heat between the two temperatures is added to the latent heat of fusion and the reaction enthalpy.

Power rate P Besides the capacity, the parameter of the power rate plays a key role and is significant for the charging and discharging time. For most of the experimental investigations, the power rate is displayed over the time and depends often on the charging state of the storage. High power rates allow fast charging and discharging, but sometimes charging and discharging curves do not have the same behavior such as latent heat TES with PCM. Determining the power rate often depends on some heat transfer characteristics between the HTF and the SM, when they are not the same fluid/material. **Charging and discharging time** t The charging time as well as the discharging time are determined by the capacity and the power rate. The losses to the surrounding can be reduced with good insulation, and can be measured or calculated for different storage temperatures and surrounding temperatures. In order to compare storage systems, energy density is a meaningful value. Attention has to be drawn to the fact that the capacity, and consequently the energy density, mainly depends on the temperature spread and level. TES systems may have the same capacity and energy density, but one is operating around 100 °C and another one at 400 °C. Exergetic efficiency may offer better comparability for this purpose.

Exergetic efficiency The exergy, the quality of heat, depends mainly on the temperature spread between the upper storage temperature to the lowest required temperature in the system. This available energy is the one to be compared when comparing different storage systems.

Additional criteria for TES evaluation: Not only technical parameters, but other criteria like economic feasibility must also be considered for comprehensive TES evaluation. The costs can be split in capital and operational expenditures, applied to the stored amount of heat over the expected lifetime and the expected operating cycles. Economic analysis of TES systems can be complex and will not be covered within this work. Environmental issues regarding the used materials may play a crucial role in TES evaluation. Toxic storage materials, insulation material, and required space all must be considered in addition to a life cycle analysis of the whole storage system.

On the other hand, energy saving criteria has to be followed. Utilities operating their efficient power plants in the night when electricity prices are low, allow to charge domestic hot water storage systems with lower primary energy input. Basically, the goal is shifting consumption from peak load to off-peak load periods. For solar thermal energy and seasonal storage, the available solar energy from the summer is used in winter for space heating and hot water demand. As mentioned above, the sizing of TES systems is important. Size is directly connected to both the capacity and the storage duration time of the storage system. Depending on the application, seasonal, diurnal, or hourly storage may lead to the desired optimization of the system. The storage efficiency is affected drastically by the storage duration. Losses are accumulated over long storage durations (seasonal), so the level of utilization decreases notably.

Degradation of thermal energy storage systems also has to be considered. The latent heat of fusion of phase change materials may decline within a certain number of cycles. In sensible storage systems the storage material possibly is effected by degradation and the grain size decreases. And all materials applied to high temperatures and fluids may be effected by corrosion. Generally, storage parameters have to be compared carefully due to a non defined standard for comparing these different technologies and applications.

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1.3. Thermal Energy Storage Methods

Different methods are available for storing thermal energy. They can be categorized into three main storage principles: sensible heat, latent heat, and thermochemical TES systems as Sharma et al. [99], Sarbu and Sebarchievici [93] and many other authors suggest. The review on thermal energy storage with phase change materials and applications from Sharma, although from the year 2009, is especially widely cited and recognized. A good review on the technology and methods for the individual TES methods is provided by Alva et al. [2]. He summarizes and explains a lot of the experimental investigations on TES for many applications. Although the main focus of this work is on phase change materials, sensible and thermochemical TES systems will be outlined briefly.

1.3.1. Sensible Heat TES Systems

In sensible heat TES systems, the storage material is present in one single phase which can be either solid, liquid, or theoretically gaseous. Charging a sensible heat TES system leads directly to an increasing TES temperature or revers. The storage capacity depends mainly on the specific heat capacity c_p of the storage material and the temperature difference between the initial temperature T_i and and the final temperature T_f as presented in Eq. (1.1). The isobaric specific heat capacity may change with the temperature, in some cases it is sufficiently accurate to calculate with the mean specific heat capacity. Sensible heat TES systems are widely spread and well developed. Because of their simple storage principle, they are the furthest developed type of storage.

$$E = \int_{T_i}^{T_f} m c_p \, dT \tag{1.1}$$

The heat transfer fluid (HTF), which is responsible for the convective heat transfer into and from the storage material, can be air, water or any other fluid. For the case of liquid storage material, the HTF can be both the storage material and the HTF. In the case of solid storage material, the heat transfer between the HTF and the storage material may be crucial for the performance of a TES system. Gaseous storage materials have low densities; therefore, large volumes or high pressure is necessary to reach high capacities. For the specific case of steam, this storage type is called Ruths-accumulator. But in general, the gaseous sensible TES systems play a minor role.

For the low temperature range beneath 100 °C and for domestic applications, water with its high specific heat capacity, availability, and non-toxicity, is a widely applied storage material. For higher temperatures, thermal oils like Therminol VP1[®], used in the thermal oil plant for the experiments in this work, are available and can be used up to 400 °C with the drawback of an inert overly and therefore system pressures of up to 16 bar. For higher temperatures, molten salts and molten metals can be used as sensible storage material and HTF, like Alva et al. explain in their review [2]. For high temperature systems, solid storage materials like rocks - thermal and chemically stable - are tested with different HTFs. Selected sensible heat TES applications and concepts are presented in the following section.

Molten sensible storage systems for CSP plants: Especially for CSP plants, TES systems play a crucial role in times of availability. With a well dimensioned TES system, a CSP plant is able to continuously produce electricity. CSP technology had its first boom around 2010, many projects constructed in the USA and Spain, after which the growth rate decreased, as the IRENA report from 2017 shows [48]. At 5 GW of installed capacity at the end of 2016, the CSP deployment remains modest, compared to other renewable technologies like solar PV with almost 300 GW of accumulated installed capacity. Almost all CSP plants under construction are built with a storage system (like presented in (Fig. 1.1), and for this application molten salt storage tanks are the stateof-the art technology. The salt applied in these systems is often a mixture of nitrates with low melting points and thermal stability for temperatures over 500 °C, as described by Bauer et al. [8]. The common solution is a two tank system, one for the hot and one for the cold salt. A challenge for this system is the auxiliary energy demand for the trace heating system for all salt containing components like pipes, valves, pumps etc.. Investigations on molten salt TES systems are trying to reduce the two tank system to a single tank system with thermocline.

Breidenbach et al. describe a single tank solution with an insulation membrane between the cold and hot layer [10]. Moreover, they present a molten tank system with filler material. The required amount of solar salt can be reduced and replaced by rocks in a packed bed, see Fig. 1.2. The molten salt serves as a heat transfer fluid and storage material at the same time while the crucial question of the height of the thermocline is tested. Breidenbach et al. provide further literature on simulations for the thermocline height for filled rock molten salt tanks [10] and Hoffman et al. provide comparisons with experiments [40]. The molten salt TES system has technically matured, and research and development is now focusing on cost reduction of the storage system.

Packed bed regenerators and waste heat: Industrial waste heat is available at multiple temperature levels and quantities all over Europe, like the Heat Roadmap Europe [78] demonstrates. In order to make use of this heat - especially those at high temperature levels - sensible TES systems with rocks as storage material and air acting as HTF could be a simple and effective solution. There are many regenerators in use, i. e. brick-flue gas regenerators in blast furnaces. At IET, packed bed regenerators filled with gravel and rocks have been under investigation for many years, and experiments with different grain sizes have been conducted like this one [96], based on [3]. There are some crucial aspects like the pressure loss over the bed height, or the geometry. For small grain sizes, the pressure loss, and hence the auxiliary energy for transporting the HTF, increases. Vertical flow through packed beds are opposed to horizontal ones with individual advantages. For vessel stability, thermal ratcheting is a key issue. Different heat expansion coefficients of the storage material and the vessel may introduce high tensions into the vessel. Besides rock, other inventive materials for packed beds are under

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Figure 1.1.: Picture of the construction side of the Figure 1.2.: Experimental investi-110 MW Cerro Dominador CSP plant in Chile with storage tank basement in 2019 [121]

gation of a molten salt TES with filler material [10]

investigation like slag, as discussed by Krüger et al. [61]. Another approach is to add phase change materials to a packed bed regenerator to stabilize the outlet temperature as Zanganeh demonstrates with experiments [124]. Beside rocks in different grain sizes, other storage technologies are considered as well for waste heat utilization. A good review is provided by Miró et al. [77].

Hot water storage systems: For lower grade temperatures, from district heating down to domestic heating, water offers great storage densities and many other advantages. Hot water storage tanks can be applied for peak shaving in district heating networks in order to reduce peak load plant operation hours - since peak load plants often burn fossil fuel. This concept was applied at the district heating network in Vienna with two pressurized storage tanks with $5600 \,\mathrm{m}^3$ storage volume each [12], presented in Fig. 1.3 and Fig. 1.4. With 6 bar tank pressure, 150 °C hot water can be stored and, as mentioned in the report, the amount of fossil fuel for peak load times in the plant was reduced. A good review on the different sensible TES systems for hot water tanks in district heating networks is presented by Dahash et al. [20]. The comparison of the different systems reveals that technologies like hot water tanks with more height than diameter offer some advantages when compared to pit TES such as better stratification, lower construction costs, etc.. The conclusion is of interest since no effective approach to evaluate one TES over another could be found. A similar issue can be seen for high temperature latent heat TES and will be discussed later.





Figure 1.3.: Construction of the storage Figure 1.4.: Picture of the of the storage tanks ©Wien Energie/EHM tanks ©Wien Energie/EHM

1.3.2. Latent Heat TES Systems

In addition to sensible TES systems, latent heat TES systems utilize the heat of fusion/vaporization to increase storage density. The storage material is subject to a phase change which can be either solid-solid, solid-liquid, or liquid gaseous. The amount of energy for the phase change is called latent heat of fusion L and is significantly higher than the sensible enthalpy for a comparable temperature range. The storage capacity for latent heat TES according to that consists of the latent heat of fusion and the sensible heat for the chosen temperature range. In practice, the lower and higher temperature level T_i and T_f are arranged around the melting point, so that the temperature difference responsible for transferring the heat is sufficient. In Eq. (1.2), the energy which can be stored in a latent heat TES is given and consists of the sensible heat below the melting point, the latent heat of fusion, and the sensible heat above the melting point.

$$E = \int_{T_i}^{T_{melt}} m c_{p,s} dT + m L + \int_{T_{melt}}^{T_f} m c_{p,l} dT \qquad T_i < T_{melt} < T_f$$
(1.2)

The specific heat c_p is not constant and differs also for solid and liquid states. For simplification, the equation sometimes is written with a mean specific heat capacity for the solid, and one for the liquid range. This and many more details will be discussed in the chapter 3.

1.3.3. Thermochemical TES Systems

Different to sensible and latent heat TES, thermochemical TES systems includes all storage concepts where at least two substances interact with each other. It includes adsorption and absorption with both, chemical and physical interaction between the substances. The amount of stored heat is related to the reaction enthalpy and is released during exothermic reaction. For the application of TES the reaction has to be reversible as it is shown in Eq. (1.3). The chemical reactant (A) together with the reaction enthalpy ΔH_r result in the two products (B) and (C).

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$$\mathbf{A} + \Delta H_r \rightleftharpoons \mathbf{B} + \mathbf{C} \tag{1.3}$$

Potential reactants for such a reaction can be carbonate, hydroxide, redox, ammonia, or organic systems, like Pardo et al. present in their comprehensive review on high temperature thermochemical TES systems [84]. Energy densities of up to 500 kW h m^{-3} can be reached, which is 5-10 times higher than with sensible or latent heat TES systems. Therefore, thermochemical TES systems can be applied to long-term storage systems such as seasonal solar thermal storage. Another advantage worth mentioning is the loss-free storing period. When the products are well separated after the endothermic reaction, they can be stored for long periods without degradation. Some of the most frequently mentioned reactions in literature are listed below in Eq. (1.4):

$$Ca(OH)_{2} \rightleftharpoons CaO + H_{2}O$$

$$CaCO_{3} \rightleftharpoons CaO + CO_{2}$$

$$6 \operatorname{Mn}_{2}O_{3} \rightleftharpoons 4 \operatorname{Mn}_{3}O_{4} + O_{2}$$

$$MgH_{2} \rightleftharpoons Mg + H_{2}$$

$$2 \operatorname{NH}_{3} \rightleftharpoons N_{2} + 3 \operatorname{H}_{2}$$
(1.4)

At present, the research focus is on the intensification of heat and mass transfers inside the reactor, and the reactor design in general. Pan and Zhao provide a good overview of the different heat storage reactors for gas-solid thermochemical hightemperature application in their work [83]. Among them, packed bed, continuous and direct type reactors were investigated, whereupon the packed bed reactor was the most extensively investigated one. Continuous and direct type reactors may have better performance, but they are still in the prototyping phase. In general, experimental and numerical approaches are rarely used for investigations on particle scale. Some of the experimental investigation is summarized by Prieto et al. for application in CSP plants [89]. They mainly mention the sulfur based cycle, metal oxides, and perovskite-form structures for the specific application. Like the other authors, Prieto et al. recommend testing the calcium carbonate cycle in industrial size because of its simplicity and the amount of research on that reaction. In general, thermochemical TES systems are highly promising, especially due to their high energy densities; but lot of work has to be done in terms of reactor design and heat transfer enhancement.

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For a structured approach, the technological challenges of latent heat TES systems are first analyzed. These challenges are called implementation barriers and they represent the main fields of research. Based on these implementation barriers, a research methodology and its aims are developed. The pathway of the experimental investigation is illustrated and individual implementation barriers are addressed. Finally, the individual papers are presented and clustered to give an overview.

2.1. Implementation Barriers

In the book from Frazzica and Cabeza [29], general requirements for latent heat TES are listed including technical, thermal and non-technical requirements. A brief summary of the requirements is provided here and discussed below.

- small volume change
- high energy density and high phase change enthalpy
- high thermal conductivity
- small subcooling
- chemical and thermal cycling stability
- high availability, low cost, non-toxic and non-corrosive

The volume change during phase transition can be a crucial topic. The difference in volume between the solid and the liquid phase can be 10% to 15% and has to be considered during construction. The storage container has to be large enough, and the PCM has to be able to expand while melting. Areas of liquid PCM without any possibility of expansion should be avoided.

The energy density is based on the PCM density, the latent heat of fusion and the lower and upper temperature of the cycle. Normally, the PCM is chosen for a specific application and then the temperature range around the melting point is selected suitable for this application. Depending on the number of available PCM in this range, the phase change enthalpy can be optimized when selecting a PCM with higher latent heat of fusion.

Thermal conductivity is one of the main drawbacks when using PCM for latent heat TES. Already in 2005, Sharma and Sagara address the topic of heat transfer enhancement in one chapter in their often cited review [100]. Many of the popular PCM for almost all temperature levels suffer from low thermal conductivity not only in the solid, but also in the liquid phase. In the liquid phase the convective heat transfer increases the heat transfer rate significantly. Thus, the heat transfer rate is usually limited by the

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heat conductivity of the solid phase. A high number of publications in the past years have focused on heat transfer enhancement; a review on performance enhancement is provided by Jegadheeswaran and Pohekar [49]. Since that review in the year 2009, many new ideas had been developed and tested by researchers such as innovative fins, macroand microencapsulation, foams, and many more. The most important ones are presented and discussed in the following chapter.

Subcooling appears when the PCM can be cooled under the solidification point - some of the paraffin show this effect by nature - without solidification. Often other reasons for subcooling can be found, such as no nucleation points in the PCM, etc. . For high temperature applications in an industrial scale, subcooling does not seem to appear in sodium nitrate in lab-scale TES (100 kg < of PCM). Another interesting question appears when modeling the phase change with subcooling and partial charging states.

Chemical and thermal stability have to be proven before applying a PCM to an industrial scale TES plant. The degradation temperature can be determined by thermogravimetric analysis (TGA); the operating temperature of the TES clearly needs be lower than the degradation temperature. Another method to detect chemical stability can be infrared spectroscopy or X-ray diffraction. Finally, the PCM has to be available, and it has to be cheap since large amounts of PCM are necessary. For interaction with other materials, corrosion tests have to be carried out.

Based on the above listed and described requirements, five implementation barriers (IB) or main fields of research can be derived.

IB1 - PCM research and development The development and characterization of new materials for PCM applications at different temperature levels is the main aspect here. New materials can include mixtures of materials with their eutectic properties and melting ranges instead of melting points. Especially for higher temperature levels the number of available materials is low.

IB2 - **Heat transfer enhancement** Improve the heat transfer performance between the HTF and the PCM, especially in the solid state because of the low thermal conductivity is aimed here. Numerous methods have been already developed and suggested in the past several years from micro to macro-scale in the scientific community to address this problem.

IB3 - **Dynamic behavior and control strategy** The highly transient power rate has to be controlled for the specific application. Interestingly, this topic is rarely targeted by researchers. This may be based on the relatively low technology readiness level so that specific applications may simply not exist yet.

IB4 - **Modeling of phase change** The melting of a PCM can be calculated analytically for only the simplest of geometries; even for two dimensional problems no analytical solutions exist. Numerical solutions can help to model the phase change, but when considering volume change, gravity, and other details, the model quickly becomes complex.

Modern computational fluid dynamics (CFD) codes can calculate geometrical domains of some centimeter size in three dimensions in acceptable time, but calculating a whole storage system is not currently possible. For system scale analysis, the storage has to be represented with reduced models, some of which are mentioned later with one main drawback, they are only valid for one individual geometry and storage type.

IB5 - **Up-scaling to full industrial scale geometries** The actual test rigs are lab scale sized - extrapolation and industrial scale experiments are necessary. When up-scaling new questions appear. The whole storage system will get heavy due to the high storage material mass. The basement and the container must be able to carry that weight and temperature, insulation is obligatory in all direction. Increasing the number of tubes may reduce the flow through the single tube and, therefore, the heat transfer rate. In addition, a high number of tubes have to be connected with inlet and overflow pipes.

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Based on the implementation barriers, a methodology and aims have been developed. Under the constraints that the focus is on mid-to-high temperature applications (>150 °C) for industrial processes, power plants and similar applications, the following aims have been defined. Some of them originate from this research project and were added later on, like the investigation on the mounting of aluminum fins on the steel tube. In brackets, the targeted implementation barrier is given for the individual aims.

1. build a lab scale prototype of a latent heat TES (IB5)

- use sodium nitrate as PCM (IB1)
- use vertically arranged longitudinally finned steel tubes with aluminum fins (IB2, IB5)
- detection of the melting behavior of a latent heat TES (IB2,IB3)
- measure power rate and capacity (IB3)
- investigate different flow direction of the HTF (IB3)

2. investigate the mounting of aluminum fins on a steel tube (IB5)

- establish a durable connection between the aluminum and the steel tube without using clamps or similar techniques on the outer diameter of the tube (IB3, IB5)
- develop a fin geometry with high heat transfer rates (IB3)
- develop a manufacturing method for bimetallic finned tubes for large-scale production (IB5)
- 3. test the combination of transversal and longitudinal fins in a test rig (IB2)
 - detect the influence of the HTF mass flow and temperature spread around the melting point on the heat transfer behaviour (IB3)
 - determine the energy balance of the test rig (IB3)

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- determine the heat transmission coefficient from the HTF into the PCM (IB3)
- test novel fin geometry with bending ear (IB3, IB5)

A lab scale prototype should help to identify the challenges for up-scaling the latent heat TES technology. Designing such a storage was supposed to gain experience for future applications. The storage material itself was not of so much of concern. It was chosen because of its melting point of 306 °C, for applications in power plants steam will be the HTF in many cases. Therefore, the live steam temperature level and the pressure level seem to be appropriate for power generation. Out of the high number of heat transfer enhancement methods, fins were chosen because of their simplicity. Finned tube heat exchangers are an industrial standard for many purposes. Vertically arranged and longitudinally finned, they allow the PCM to melt and expand immediately to the top of the storage - assuming that the fins stick out a little from the solidified PCM. The position of the melting front is content to many numerical, but also experimental investigations. We aimed to detect the melting front with temperature sensors in the PCM. With sensors in the HTF, the power rate and the stored energy will be calculated.

Out of the first prototype, the topic of mounting of aluminum fins on a steel tube arose. The used hinge bold clamps for the first test rig do not allow hexagonal cross section without huge gaps between the tubes. For an optimal spatial arrangement, the connection of the aluminum fins on the steel tube should not happen on the outer diameter of the fins. Additionally a durable connection between the steel tube and the aluminum fins has to be guaranteed over the whole operation temperature range and the lifetime. A novel connection design for bimetallic finned tube will be developed and tested.

Before testing the new bending ear, another novel combination of transversal and longitudinal fins will be tested in a new lab scale test rig. With mass flow and temperature spread variation and a high number of testing points a lot of data should be recorded and performance improvement should be detected. For this new geometry, the heat transmission coefficient will be determined and presented in Paper 8.

2.3. Paper Overview

As presented in Fig. 2.1, the chronological development of the research is illustrated with the publications and the main research topics. All together, two test rigs were erected, one in 2013 (Paper 1 and 2) and one in 2018 (Paper 6, 7 and 8). In between, the experimental investigation on bimetallic finned tubes took place (Paper 3, 4 and 5)). A comprehensive description of the main topics is provided within this section, together with the paper abstracts of the papers published in journals. Out of the eight publications three (Paper 2, 5 and 8)) were published in a journals, the others in conference proceedings, all of them underwent a peer review process.

All own publications are available in the appendix A in the print-version of this thesis.

2.3. Paper Overview



Figure 2.1.: Chronological overview of the papers and research topics

2.3.1. Finned Mono Tube Latent Heat TES, Paper 1 and 2

Following the methodologies first aim, a lab-scale test rig for a latent heat TES with 300 kg of sodium nitrate as PCM is presented. The shell and tube heat exchanger is a vertically arranged shell tube with aluminum fins to increase the heat transfer into and from the PCM. The melting behavior is presented and temperature trends for charging and discharging cycles are shown. Besides the characteristic storage parameters, the flow direction influence was part of the investigation. With plain longitudinally finned vertical tubes the flow direction of the HTF (from the top or bottom) makes a difference in melting time.

The first experimental result were published at the ASME 2014 8th International Conference on Energy Sustainability in Boston, MA and mentioned as Paper 1 within this work [113]. More detailed results were presented in the Journal of Energy and Power Engineering No. 8 from 2014, this publications is called Paper 2 and is listed in the bibliography as [114] within this thesis.

Abstract Paper 2 The present experimental investigation covers the construction of a LHTES (latent heat thermal energy storage system), which uses $NaNO_3$ (sodium nitrate) as PCM (phase change material). The storage unit is filled with 300 kg of the PCM. For the heat transfer, a vertically arranged bimetallic mono tube with longitudinal fins is

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used. The fins increase the heat flux into/from the PCM. Thermal oil is used as a heat transfer medium, as it allows a working temperature up to 400° C. This thermal energy storage is able to store $60 \, kWh$ of thermal energy and can be loaded with a power up to $20 \, kW$.

One part of the investigation results presented in this paper was the determination of the storable energy and the comparison with data from literature and calculations. Additionally, the melting behavior of the PCM was measured with temperature sensors located at different positions over the height of the storage unit. Finally, the entrance of the heat transfer medium was changed from the top to the bottom of the thermal energy storage unit and a different melting behavior could be detected.

2.3.2. Bimetallic Finned Tube Design, Paper 3, 4 and 5)

For the lab scale test rig built before, the aluminum fins were split into six parts and fixed with a hinge bold clamp on the steel tube. This comes along with the disadvantage of non-hexagonal cross section - the arrangement of many finned tubes will not be as efficient as with hexagonal cross section. Therefore, a new fastening method was developed, following the second aim of the methodology. With this method, hexagonal cross sections are realizable and the manufacturing can be automated.

The two conference proceedings, Paper 3 from the ASME 2015 9th International Conference on Energy Sustainability in San Diego, CA [115] and Paper 4 from the 10th Conference on Sustainable Development of Energy, Water and Environment Systems - SDEWES 2015 [112] form the foundation for Paper 5 which was published in the Energy Conversion and Management Journal Vol. 125 in 2016 [111].

Abstract Paper 5 Based on the high energy density of phase change materials, latent heat thermal energy storage devices can play an important role in the future energy market. Therefore, the latent heat thermal energy storage technique is an interesting technology for industrial applications (e.g. batch processes) and power cycles. A key technology for such a storage device is the design of the heat exchanger tube, because the heat transfer rate by charging and discharging is the limiting factor based on the low thermal conductivity of the phase change material. The heat exchanger tube material used for such an application should have a high thermal conductivity and also a high mechanical resistance. Such a behavior can be found in a combination of different materials.

The present paper deals with the design of such a heat exchanger tube composition consisting of a plain steel tube and an aluminum tube where fins can be attached. A novel bimetallic tube composition is presented and compared with three common compositions. First, the mechanical stability of the bimetallic compositions was determined. Additionally, a creep test of the used aluminum under operation conditions for a storage device using sodium nitrate as phase change material confirmed its ability to be used for the operation in a latent heat thermal energy device. One of the main challenges for the compositions under investigation is based on the different thermal expansion coefficient for aluminum and steel, which results in different strain and creeping tendencies of the aluminum at operation temperature of the storage system, which is up to $340^{\circ}C$. A good heat transfer from the heat transfer fluid through the steel tube to the storage material around the fins can only be guaranteed through a close and stable connection between the two tubes.

Compared to former solutions, the fin circumference and the fin design are independent from the connection to the steel tube and allows individual arrangements of tubes and high packing densities. The experimental investigations have shown that the novel bimetallic tube composition is able to compensate these different strains and is capable of guaranteeing a stable connection between the steel and the aluminum tube. This high pressure and high temperature resistant bimetallic heat exchanger tube is easy to assemble and may play a key role for the development of thermal energy storage and other heat exchanging processes.

2.3.3. Novel Fin Geometry, Paper 6, 7 and 8)

Based on numerical simulations which where conducted simultaneously, the combination of transversal and vertical fins together seemed promising. Another test rig was built with the novel fin geometry and many more temperature sensors in order to determine the melting behavior more accurate (aim number 3 in the methodology).

This investigation is published in Paper 6 at the 13th Conference on Sustainable Development of Energy, Water and Environment Systems - SDEWES 2018 [97] and in Paper 7 in the proceedings of the 4th Thermal and Fluids Engineering Conference (TFEC 2019) [94]. In Paper 8, the heat transfer in the new test rig was examined and a heat transmission coefficient was calculated. This results were published in the journal Energies Vol. 12 No. 7 in 2019 [95].

Abstract Paper 8 Thermal energy storage systems with phase change materials promise a high energy density for applications where heat is to be stored in a narrow temperature range. The advantage of higher capacities comes along with some challenges in terms of behavior prediction. The heat transfer into such a storage is highly transient and depends on the phase state, which is either liquid or solid in the present investigation. The aim is to quantify the heat transfer into the storage and to compare two different fin geometries. The novel geometry is supposed to accelerate the melting process.

For this purpose a single tube test rig was designed, built, and equipped with aluminum fins. The phase change material temperature as well as the heat transfer fluid temperature at the inlet and outlet were measured for charging and discharging cycles. Sodium nitrate was used as phase change material, the storage was operated $\pm 30^{\circ}C$ around the melting point of sodium nitrate, which is $306^{\circ}C$.

An enthalpy function for sodium nitrate is proposed and the methodology for determining the apparent heat transfer rate is provided. The phase change material temperature trends are shown and analyzed, different melting in radial and axial directions and in the individual geometry sections occurs. With the enthalpy function for sodium nitrate,

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the energy balance is determined over the melting range. Values for the apparent heat transfer coefficient are derived, they allow capacity and power estimations for industrial scale latent heat thermal energy systems.

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3. Phase Change Phenomena and Materials

3.1. Phenomenological Approach

Phase change materials undergo a phase transition within their operating range as defined in Fleischer's research [27]. During phase change, the material absorbs energy from its surrounding without a change in temperature. The absorbed energy increases the energy of the constituent atoms or molecules and increases their vibrational state. For the solid-liquid phase change, this is displayed schematically in Fig 3.1. The amount of energy needed for the transition is called latent heat of fusion for the solid-liquid transition, and it is called latent heat of evaporation for the liquid-gaseous phase change.

A continuous heating process exemplar is shown in Fig. 3.2. The heating of the solid material begins and the temperature increases immediately, due to the sensible heat of the material, until the melting temperature is reached. Additional heat will start the melting process, the temperature remains until the material has reached the liquid state. Further heating raises the temperature depending on the specific heat capacity in the liquid state, until the boiling point is reached. Further heating leads to vaporization, the temperature begins to increase again when the material is gaseous. Additional heating will produce superheated vapor. Often, the latent heat of vaporization is higher than the latent heat of fusion. For thermal applications, the volume change over the transition is crucial, a high latent heat often competes with high changes in volume. For this reason, the liquid-gaseous phase change often is unfeasible.



Figure 3.1.: The melting/solidification process [27]



Figure 3.2.: Standard heating curve [27]

3.1.1. Solid-Liquid Phase Change

The solid-liquid phase change is the phenomena that most latent heat TES are based on. Of all phase transitions, solid-liquid phase change comes with a minor change in volume, especially when compared to the liquid-gaseous phase transition which is intensively studied for water/vapor in steam power cycles. The solid-solid phase change will be discussed in chapter 3.1.3, and is a relatively new area of focus for applications in CSP plants with most of the research papers dating back to the last few years.

When the majority of the energy is used for the phase transition, the devices are named latent heat TES, thermal capacitors, or similar, compared to sensible or thermochemical storage systems. Even so, there is usually a portion of the stored energy which remains sensible heat, as Eq. (1.2) points out. The Energy is split into the sensible part below the melting point, the latent heat of fusion and the sensible heat above the melting point. This energy storage principle is the same for seasonal ice storage which has been used for ages and the high temperature latent heat TES for CSP applications [14].

As Fleischer describes in her book [27], melting is a highly transient process. Based on the considered volume, the boundary conditions contain a heat source, and often, a heat loss to the surroundings. The volume itself is either solid, liquid, or divided in between. This ratio is often called liquid fraction γ and is between 0 (solid) and 1 (liquid). The border between the liquid and solid volume is called the melting front. The evolution of the melting front depends on the heat transfer in the solid and liquid fraction. While in the solid volume only heat conduction occurs, in the liquid fraction convectional heat transfer increases the heat transfer coefficient at the melting front. Natural convection appears in the liquid PCM. So, the prediction of the melting front and its evolution is complex, as Fleischer points out.

$$E = \int_{T_i}^{T_{melt}} m c_{p,s} dT + m \gamma L \qquad T_i < T_{melt}$$
(3.1)

The stored energy E can be expressed with equation (3.1) for partial molten PCM at melting temperature. The liquid fraction corresponds to the mass fraction proportion between the liquid and the total mass and is shown in equation (3.2).

$$\gamma = \frac{m_l}{m_l + m_s} \tag{3.2}$$

Besides its application in TES systems and thermal management with PCM, the solid-liquid phase change, more precisely the liquid-solid phase change, plays a major role in casting technology research. The solidification of metals during casting is the principal topic in the book from Stefanescu [104]. The topic of solidification of metals is well investigated since casting is one of the basic production process technologies in manufacturing. The main difference of PCM for TES may be the heat conduction coefficient, although even metals as PCM have been discussed in the past years. The theory of solidification involves different scales, from nucleation on the nanoscale to transport phenomena on the macro scale. Compared to single PCMs, metal alloys consist of different substances and form different states of equilibrium. Furthermore, different cooling rates can lead to subcooling and a huge variety in crystal structures. It would be interesting to investigate whether approaches from casting technology can be used for PCMs and their application in TES systems.

3.1.2. Liquid-Gaseous Phase Change

Volume expansion during vaporization is a significant challenge in using liquid-gaseous phase change for TES applications. This is the main reason why this phase change mechanism seems unsuitable for storage applications. The heat of evaporation in contrast to the latent heat of fusion would be high; for water it is about 2257 kJ kg^{-1} compared to 333.5 kJ kg^{-1} , respectively. Nevertheless, the topic of vaporization and condensation (especially with regards to water) has been widely investigated because of steam power plant processes. Kulacki dedicated a chapter in his Handbook of Thermal Science and Engineering [63] to heat transfer with phase change. The application of the liquidgaseous phase change is not yet reported for storage applications.

However, the so called Ruth's accumulator is mentioned in this context. The device basically consists of a steam drum, and it is capable of storing steam under high pressure and temperature. The challenge is found in up-scaling this concept since the wall thickness for large diameters must be huge and material costs are normally high for this type of storage. In their paper, Gonzales et al. compare the application of direct and indirect molten salt storage tanks with Ruth's accumulators for their use in a CSP plant [34]. For short storage times (<3 h), the Ruth's accumulator seems to be more cost effective when compared to sensible molten salt tanks. Another interesting application is mentioned in the research done by Hofmann et al. [41] and Dusek et al. [23]. The capacity of a Ruth's accumulator can be increased effectively by adding a PCM layer to the outside of the accumulator. In summary, the effective use of liquid-gaseous phase change for storage application of Ruth's accumulators as short term storage in processes which utilize steam.

3.1.3. Solid-Solid Phase Change

The terminology of phase change is comprised of the well known states of solid, liquid, gaseous, and plasma. However, a phase transition from solid to solid can be observed on a nano-scale level for some materials. The arrangement of atoms changes during a solid-solid phase transition between two solid crystalline or semi-crystalline phases, e.g. monoclinic to cubic. This structure transition happens at a specific temperature, and the effect is comparable to the well known solid-liquid phase change. Different materials show these effects, as Bayon et al. demonstrated [9] in reference to lithium and sodium sulfates. In this investigation, different mixtures of sodium and lithium sulfate were investigated with differential scanning calorimetry, high temperature Insitu X-ray diffraction and thermogravimetric analysis. The aim was to determine the phase transition temperatures, enthalpies, the specific heat capacities, and the crystalline phase composition. Based on the measured data, an economic assessment was applied to

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Figure 3.3.: CSP concept with solid-solid PCM TES with CO₂ Brayton cycle [9]

the different mixtures. A mixing ratio of 59.17%, NaLiSO₄ and 40.83% LiSO₄ seemed to be promising. With the adaption of the mixing ratio, different melting temperatures can be adjusted. They allow the combination of different PCMs and lead to a cascaded PCM storage system which is presented in figure 3.3.

Compared to the solid-liquid phase change, the solid-solid transition has some advantages that are worth mentioning. The abidance in the solid state avoids leakage and there is no need for encapsulation, no segregation is necessary (as it is with additives such as copper particles to a PCM), and smaller changes in volume are all advantages discussed by Fallahi et al. in their review [26]. Depending on the molecular structure of the material, different solid-solid phase transitions exist and lead to a high variety of transition enthalpies and temperatures as well as different heat conductivity values. In closing, the research into the TES application of solid-solid phase change is still in its infancy and brings with it new challenges.

3.2. Phase Change Materials

There are many different materials which are able to be used in phase change applications, some of which are already commercially available. These materials can be clustered into three main categories: organic PCMs which are widely spread and are often topic of research because of their lower application temperature; inorganic PCMs which often have higher melting temperatures; and, finally, metallic PCMs. The clustering often depends on the main focus of the literature. While Dincer and Rosen [21] describe organic PCM exclusively with a focus on household heating systems, Fleischer [27], Frazzica and Cabeza [29] and Cabeza and Tay [14] follow a wider approach with an additional focus on high temperature systems.

3.2.1. Organic PCMs

Organic PCMs are the most popular PCM type, and they include many different materials such as paraffin, fatty acids, sugar alcohols, plastics, etc. . They are the most numerous group of PCMs with highly diversified properties. The main subgroups are mentioned here:

Paraffins Paraffins are the most used and commercially available PCMs. This alkane type compound (C_2H_{2n+2}) has melting temperatures between 0 °C and 120 °C. The melting temperature can be adjusted by the chain length, and they show good energy densities and compatibility with metals. Compared to other organic PCMs, Paraffins do not show subcooling, but their melting point often corresponds to a melting range. In the solid state, Paraffins are waxy. They are obtained from petroleum distillation and are a combination of different hydrocarbons. Further advantages mentioned in the review from Sharma and Sagara [100] are that they have no tendency to segregate, and they have chemical stability. Disadvantages of Paraffins may be their low thermal conductivity in the solid state, and their high volume change and flammability. Examples of paraffins are Octadecane $(T_m = 29 \,^{\circ}\text{C}, L = 244 \,\text{kJ kg}^{-1})$, Tricosane $(T_m = 48.4 \,^{\circ}\text{C}, L = 302.5 \,\text{kJ kg}^{-1})$ or Tetracosane $(T_m = 51.5 \,^{\circ}\text{C}, L = 207.7 \,\text{kJ kg}^{-1})$ [27]. Material properties can vary greatly depending on the literature source. Sharma and Sagara i. e. provide much higher values for the latent heat for Tetracosane $(T_m = 51 \,^{\circ}\text{C}, L = 255 \,\text{kJ kg}^{-1}).$

Fatty acids The fatty acid compounds in the form of $CH_3(CH_2)_{2n}COOH$ tendentiously have lower melting points than paraffins and this enables applications in the building sector. A comprehensive list of fatty acids is provided in [100]. Fatty acids are more expensive than paraffins, and often do not have sharp melting points. Fatty acids which deserve some mention are: Capric acid $(T_m = 32 \,^{\circ}\text{C}, L = 153 \,\text{kJ}\,\text{kg}^{-1})$, Lauric acid $(T_m = 44 \,^{\circ}\text{C}, L = 178 \,\text{kJ kg}^{-1})$ and Stearic acid $(T_m = 69 \,^{\circ}\text{C}, L = 202 \,\text{kJ kg}^{-1})$ [27].

Sugar alcohols Sugar alcohols are organic compounds derived from sugars that comprise a class of polyols. Their advantage is a high latent of fusion as Sole et al. explain in their research [101]. Their main disadvantage is oxidation so that their storage has to be operated in an inert atmosphere. Erythritol ($T_m = 120 \,^{\circ}\text{C}$, $L = 340 \,\text{kJ kg}^{-1}$ [101]), for example, has high latent heat of fusion and an interesting temperature level for solar thermal district heating. Besides oxidation, thermal hysteresis also seems to be challenging when utilizing sugar alcohols.

Plastics Plastics, like high density polyethylen (HDPE) or polyamids (PA), are under investigation as PCMs. Experimental investigations like those done by Zauner et al. [126], demonstrate their potential as PCMs for temperature levels between $105 \,^{\circ}$ C and $155 \,^{\circ}$ C. Another review on plastics as PCMs for temperature ranges between $120 \,^{\circ}$ C and 200 °C was completed by Gasia et al. [30] and concludes that HDPE offers high potential as a PCM. Crucial factors may be the non-sharp melting range of plastics, their flammability, and their high viscosity.

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3.2.2. Inorganic PCMs

The category of inorganic PCMs is mainly comprised of salts and salt hydrates. The melting points of salt hydrates range from 5 °C to 130 °C. Salts have higher melting temperatures between 150 °C and 800 °C. Inorganic PCMs cover a wide range of temperature levels with individual properties and challenges.

Salt hydrates Salt hydrates combine inorganic salts (oxides, carbonates, sulfates, nitrates and halides) with water and they form compounds with $n \cdot H_2O$. Salt hydrates have three dimensional structures open for water molecules to fit into the crystal lattice. Different crystal structures exist, and some are more open to water than others. Salt hydrates have sharp melting transitions compared to some organic PCMs, and have generally high latent heat of fusions. Disadvantages of salt hydrates are their subcooling and corrosive behaviors. A comprehensive review on salt hydrates for latent heat storage systems is provided by Kenisarin and Mahkamov [55]. 18 different salt hydrates, all market available, are presented along with their thermophysical properties and costs. The conclusion is about missing standards in determination of the thermophysical properties. Besides their application as latent PCM, salt hydrates are often utilized as thermochemical energy storage materials using their hydration and dehydration reaction. A review for this application is presented by Trausel et al. [109].

Salts The properties of salts are similar to the properties of salt hydrates, except that salts do not show phase segregation when used as a pure substance. Compared to organic PCMs, salts have higher densities which means higher energy densities. The compatibility with container material has to be checked before applying salt to a storage tank. The main advantage of salts is their great applicable temperature range, their unique selling point. In temperature levels around 300 °C, sodium or potassium nitrate are potential PCM candidates (NaNO₃ or KNO₃). Fleischer [27] mentions the high propensity towards subcooling of inorganic PCMs. The experimental investigations carried out at IET with sodium nitrate do not support this position - at least not for sodium nitrate and large storage sizes of 100 kg of PCM. This may predicate on the impurities of the PCM and, therefore, the high number of potential nucleation particles. The main aspects of salts can be summarized as follows [75]:

- wide applicable temperature range (150 °C 800 °C)
- high latent heat of fusions
- higher heat conductivity than organic PCMs
- subcooling is possible but only a few K
- low vapor pressure

Tables of salts for application in a TES are provided by many authors. Some examples are the books [27], [29], [14] and [75]. Good reviews are also carried out by Sharma and Sagara [100], Gil et al. [32], Maldonado et al. [74], and Nazir et al. [80]. In Fig. 3.4, a selection of salts and mixtures is presented with melting points higher than 150 °C.



Figure 3.4.: PCMs for latent heat TES with temperatures higher than 150 °C from [29]

Nitrates are marked red, chlorides blue, and mixtures black. The total energy stored per unit cost is shown over the melting points.

3.2.3. Mixtures, Metals and Other PCMs

Mixtures and Eutectics Mixtures are possible between inorganic, organic, or in between these groups. Mixtures can improve the properties of any PCM so it fits the desired application. A famous mixture is the so-called solar salt, a 60% NaNO₃ and 40% KNO₃ eutectic mixture with a melting point around 222 °C. The primary use for this mixture is sensible TES in molten salt tanks. Mixtures between the two salts are well investigated. When mixing two salts in non eutectic mixtures, the melting temperature modifies to a melting range depending on the composition.

Metals Metals are unusual PCMs and the many reasons for this are accentuated in Fleischer's work [27]. One such reason is their relatively low heat of fusion. The low melting point metal Gallium ($T_m = 29.8 \,^{\circ}$ C) has only $80 \,\text{kJ kg}^{-1}$; others are in the same range, or even lower. Advantages of metals are their high thermal conductivity, which makes heat transfer easy, and their high density still leads to useful energy densities. Corrosion may be a topic, since gallium e.g. reacts with aluminum and copper. A comprehensive review on low temperature metals is provided by Ge et al. [31]. As they point out, the application of metal based PCMs for low temperature applications has been significantly ignored in the past decades - they believe this to be wrong. For high temperature applications, metals are one of the few available materials. Aluminum and

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Figure 3.5.: Schematics of a heat flow DSC with a disk type sensor - heat flow paths from [65]

other metals have excellent heat conductivity, but this comes along with high specific costs and inter-metallic corrosion when using metal containment.

Water-salt solutions For cooling applications, water-salt solutions can be the PCM of choice since the melting points are below 0 °C. Due to the properties of water, they have high energy densities, and phase segregation can be aided when using eutectic mixtures. A good review on PCM for cold TES applications is provided by Oro et al. [81].

3.3. Methods for Thermal Characterization of PCMs

The thermal properties of PCMs are one of the main design criteria for latent heat TES. Based on their characteristics, the whole system can be designed. Critical design values include the latent heat of fusion L, the melting temperature T_m , the specific heat capacity c_p , and the heat conductivity λ . Several methods are available to determine these parameters for individual materials, the most common ones are presented here.

3.3.1. Differential Scanning Calorimetry Measurements

According to Lager [65], differential scanning calorimetry (DSC) measurement is the most commonly used method to determine the exchange of heat. Several parameters can be obtained with DSC measurements; among them are the specific heat capacity, the latent heat of fusion, the melting temperature, and the chemical reaction enthalpy. Basically, two different type of DSC measurements are available, the heat flux and the power compensated measurement.

As presented in Fig. 3.5, the two crucibles in the furnace can be filled with substances. If both samples have the same thermal behavior while heating the furnace with the desired heating rate, the temperature of both samples will be similar and no heat flux between the two samples will occur. For the case of different samples, a temperature gradient and, therefore, an electrical voltage from the attached thermocouples can be


Figure 3.6.: Voltage U_{DSC} versus temperature T during a transition with the characteristic temperatures from [65]

measured. In order to gain meaningful results with DSC, calibration has to be carried out. Furthermore, the heating and cooling rate, the type and size of the crucibles, the position of the sample in the crucible, the mass and size of the sample, and the thermal contact between crucible and sensor all play a role and must be taken into consideration. Temperature, heat, and heat flow calibration have to be done before starting measurements, as Lager explains [65]. A schematic phase transition measurement is presented in Fig 3.6 with the initial and final temperature T_i and T_f , the extrapolated initial and final temperatures $T_{e,i}$ and $T_{e,f}$, and the peak temperature T_{pk} .

Challenges with DSC measurements As mentioned above, several factors potentially influence the result of DSC measurements. The heating rate β is among them. Like Lager describes, the peak temperature T_{pk} changes with the heating rate. Based on defined measurement protocols, the heating rate for phase transition tests should be reduced until the change in the peak temperature is < 0.2 K. Other standards like DIN EN ISO 11357-4 recommend for the heat rate values of 10 K min⁻¹. Tests with the commercially available Rubitherm *RT70HC* with two different heating rates of (a) 0.25 K min⁻¹ and (b) 10 K min⁻¹ show diverging results. While the extrapolated initial temperatures are similar for (a) 70.0 K and (b) 69.7 K, the extrapolated final temperature diverge significantly between (a) 72.0 K and b) 79.9 K. The latent heat of fusion result in (a) 228.1 kJ kg⁻¹ and (b) 243.5 kJ kg⁻¹. Beside the differences, the uncertainty of the measurements has to be observed. Generally, lower heating rates produce higher uncertainties, for the case of a heating rate of 0.25 K min⁻¹ the uncertainty is as high as 10.5 % compared to 3.3 % for the higher heating rate (β).

3.3.2. Measuring Thermal Conductivity

Laser flash apparatus (LFA) The laser flash apparatus consists of a sample in the form of a slice. From one side, a short laser pulse raises the temperature. With an infrared radiation sensor, the temperature field on the other side of the sample is measured. As

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long as there are no chemical reactions and phase transition (heat source and sinks) this methods offers some real advantages. The thermal contact resistance problem does not occur, and the surface heat losses are minimized through the short measuring duration. As Lager describes in his thesis [65], modern LFA systems have highly sensitive IR detectors, energy controlled laser or light beam, gas inlets, controlled vacuum conditions, and different furnaces for broad temperature ranges. In his experiments he measured the thermal diffusivity of Rubitherm RT70HC which ranges between $0.17 \text{ mm}^2 \text{ s}^{-1}$ and $0.23 \text{ mm}^2 \text{ s}^{-1}$ in the solid phase and $0.13 \text{ mm}^2 \text{ s}^{-1}$ to $0.19 \text{ mm}^2 \text{ s}^{-1}$ for the liquid phase.

Transient Hot Bridge (THB) The transient hot bridge measures the thermal conductivity based on a thermoelectric sensor. The THB method is developed from the transient hot strip based on electrical conducting strips which can act as joule heaters and resistance thermometers. The sample is heated with a constant current and the sensor is placed into it. The voltage over the thermal resistance of the strip is measured and, due to the changing electrical resistance, the signal can be used to evaluate thermal conductivity. Like other methods, the THB has to be calibrated using reference materials. The THB sensors are positioned between two blocks of material and from the measured signal the conductivity can be determined. For more details regarding the THB method, see [36] for reference.

3.3.3. Other methods for determining thermophysical properties

For the determination of thermal conductivity, the hot flow meter (HFM) represents a steady state method for conductivities up to $2 \text{ W m}^{-1} \text{ K}^{-1}$. The test set-up consists of a hot and a cold plate which are both temperature controlled. The sample is positioned between these plates. For measuring the heat flow over the plate, an equilibrium has to be reached.

The push rod dilatometry is a method to determine the linear thermal expansion coefficient of a solid as a function of the temperature. A sample is placed in the furnace on a sample carrier and the thermal expansion is measured with a displacement transducer over a push-rod. All used materials expand so correction functions have to be applied to the results. Both methods are explained well by Lager [65].

3.4. Sodium Nitrate (NaNO₃)

Sodium nitrate was used as phase change material in the experimental investigations carried out at IET. For this reason, a closer look at the material and its properties is necessary. Sodium nitrate is a crystalline salt, inorganic, and solid at room temperature. It has a white or colorless appearance and a molar mass of $84.99 \,\mathrm{g}\,\mathrm{mol}^{-1}$. It is hygroscopic and soluble in water. Its main applications are in fertilizer production and industries such as the glass industry, explosives, etc. . It occurs in natural deposits, but is also produced synthetically at a large scale.



Figure 3.7.: Platinum calorimetry of sodium nitrate from 1909 [35]

The determination of the thermophysical properties of salts dates back to the 19th century. One of the first publications examining the properties of salts is provided by Goodwin and Kalmus in 1909 [35]. They describe an apparatus for measuring the specific heat capacities and the latent heat of fusion for salts up to a temperature of 600 °C, and remark upon the unreliable data availability at that time.

In Fig. 3.7 the heat temperature plot for NaNO₃ from the year 1909 is presented. The temperature is given in degree Celsius and the heat in calories. The latent heat of fusion of 45 calories corresponds to 188 kJ kg^{-1} which is remarkably accurate considering the measurement methods at that time.

Some years later, Kracek investigated inversions from one crystalline modification of sodium nitrate to another. Inversions of this type come with a change in the crystal lattice - today from a TES perspective the solid-solid phase change. Kracek et al. dedicated two publications to the gradual transition of sodium nitrate ([59] and [60]). They described the transition at 275.5 °C which happens rather gradually, and in the second paper they dealt with the crystal arrangement and used powder diffraction. In any case, the solid-solid transition of sodium nitrate at 275.5 °C involves small amounts of enthalpy compared to the solid-liquid phase change at the melting temperature.

Measurements with modern DSC methods were realized by Carling in 1983 [17], Takahashi et al. in 1988 [105] and Jiriri et al. in 1995 [54] for sodium nitrate and potassium nitrate. Takahashi et al. included lithium nitrate while Jiriri et al. chose cesium nitrate. All determined the heat capacities and the latent heat of transition for the mentioned salts. Data from Carling is applied for modeling the phase change in the following chapter because he published the apparent specific heat capacity from DSC measurement over the whole phase transition.

3.4.1. Thermophysical Properties of Sodium Nitrate

The most comprehensive review and thermophysical investigation on sodium nitrate is provided by Bauer et al. ([6] and [8]). These reports measured and compared the different

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properties of sodium nitrate with many values from literature. Among the mentioned properties, the melting temperature, the latent heat of fusion, the thermal diffusivity, the heat capacity, and the density are displayed in Fig. 3.8.

Melting temperature and latent heat of fusion The melting temperature is stated as $306 \,^{\circ}\text{C}$ and the latent heat of fusion is given as $178 \,\text{kJ} \,\text{kg}^{-1}$, event though values in literature differ. A comparison is provided in Paper 1. These mentioned values are applied for data analysis of the experiments conducted in this thesis. For the solid-solid phase transition around $275 \,^{\circ}\text{C}$ and values from $12 \,\text{kJ} \,\text{kg}^{-1}$ to $45 \,\text{kJ} \,\text{kg}^{-1}$ are reported.

Thermal stability and nitrite formation Sodium nitrate tends to form sodium nitrite at higher temperature levels. Even small amounts of nitrite can influence the thermophysical properties of sodium nitrate, as Bauer describes in his work. Long term tests of NaNO₃ at 350 °C and higher temperatures have been carried out in order to investigate the nitrite formation. The decomposition of sodium nitrate can be categorized into three stages. Below 450 °C there is little nitrate formation, between 450 °C and 550 °C a nitrate-nitrite equilibrium can be observed, and over 550 °C decomposition with a release of nitrogen oxides was detected. A 4% molar mass ratio of sodium nitrite in sodium nitrate can lead to a decrease of the melting temperature and lower enthalpy of fusion. The exposure of sodium nitrate to temperatures around 500 °C for some ten hours will lead to approximately 4% molar mass ratio, as reported by Bauer. As a result of this investigation, the maximum storage temperature for latent heat TES with sodium nitrate as PCM has to be limited to 450 °C. Since the experiments operate in a temperature range of 20 °C - 40 °C around the melting point, i.e. between 266 °C and 346 °C, nitrite formation is not a problem.

Density and thermal expansion coefficient The density of sodium nitrate is about 2260 kg m^{-3} at 25 °C. The density decreases slightly until the solid-liquid phase transition occurs. The volume change at the melting point is averaged from literature values and is about 9.7%. Further heating leads to decreasing density values, as expected. The linear thermal expansion coefficient is provided with $40 \times 10^{-6} \text{ K}^{-1}$ at room temperature, increasing until the solid-solid transition at 275 °C [44]. As a design criteria of the PCM storage tank, the crucial value is the volume change during melting - this additional volume has to be considered.

Heat capacity The specific heat capacity of sodium nitrate has been measured by various authors. It increases with the temperature and has basically two peaks which can be seen in the trend in Fig. 3.8. The first peak at 275 °C at the solid-solid transition and the main peak at 306 °C, the melting. For the solid phase, the heat capacity can be approximated with a linear function. For the liquid phase, the heat capacity can be considered constant with a value of $1.655 \text{ kJ kg}^{-1} \text{ K}^{-1}$.

Thermal diffusivity and conductivity Thermal diffusivity can be obtained by several measurement techniques such as the hot-wire method, optical techniques, and stepwise heating and laser flash methods (the last method is used in Bauer's work). In general, thermal diffusivity as well as conductivity can be determined for the liquid phase precisely as shown in Fig. 3.8. Most authors report values around $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ for the heat conductivity and $0.15 \text{ mm}^2 \text{ s}^{-1}$ for the thermal diffusivity. For the solid phase, the values scatter so much so that no reliable values can be reported. The correlation between the thermal conductivity and the thermal diffusivity is given in Eq. (3.3); the measurements can be crosschecked with that equation.

$$a = \frac{\lambda}{\rho \, c_p} \tag{3.3}$$

3.4.2. Material Compatibility and Corrosion

Due to the low thermal conductivity of sodium nitrate, and the majority of PCMs in general, enhancing its heat transfer ability is widely discussed. With respect to these enhancements, it is crucial to consider the applicable material's compatibility with sodium nitrate. All materials which come into contact with sodium nitrate, including those materials used to enhance its heat transfer abilities, may be affected by corrosion.

Steel The containment vessel and the tube are made of carbon steel. Steel of varying types is normally used for nitrate and nitrate mixtures according to the Metals Handbook of Corrosion [58]. The basicity of the melt normally prevents iron corrosion. Stainless steels show low corrosion rates in salt-mixtures comparable to pure sodium nitrate. For the mixture of NaNO₃-NaCl-Na₂SO₄ with 86.3 mol%, 8.4 mol% and 5.3 mol% respectively, the corrosion rate for carbon steel is mentioned with 15 µm yr⁻¹. This is supported by our observations with carbon steels in sodium nitrate latent heat TES. For lab-scale sized TES systems, carbon steel seems to be sufficient.

Aluminum Aluminum fins applied on the steel tube are in direct contact with the solid and liquid sodium nitrate in the storage system. In his book called, Corrosion of Aluminium [116], Vargel describes, that these nitrates (sodium, potassium and ammonia) in molten form have no action on aluminum. The application of aluminum fins is recommendable.

Selected other combinations and references Cabeza et al. [13] investigated the corrosion of stainless steel, steel, aluminum, copper and brass in combination with two salt hydrates (sodium acetate trihydrate and sodium thiosulfate pentahydrate) within the temperature range of 48 °C and 58 °C. As a result of this investigation, steel and aluminum are recommended; although, steel has to be checked in detail. Brass and copper are not recommended at all.

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Figure 3.8.: Thermophysical properties of sodium nitrate from [8] (k corresponds to the thermal conductivity in the nomenclature of this source)

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Other studies from Oro et al. [82] and Moreno et al. [79] investigated the corrosion rate of steel, stainless steel, copper, aluminum and polymer combinations with different PCMs. The chosen PCMs focused on domestic heating and cooling applications and cold storage systems, and among them were many salt hydrates. The conclusion was similar in both investigations: aluminum, copper, and carbon steel show high corrosion rates (several hundred mg cm⁻² yr⁻¹), and the only applicable material for the selected PCMs (not sodium nitrate) seemed to be stainless steel.

Qiu et al. [91] used higher temperature levels to test the suitability of stainless steel 316L and Inconel 625 for their application in a latent heat TES with a eutectic NaCl–NaF mixture. The steels were exposed to a temperature of 780 °C for 100 h and 2500 h. The melting temperature of the applied PCM was at 680 °C. Both demonstrated low corrosion activity, and the Inconel 625 seems appropriate for long term operation.

Similar tests using sodium nitrate and steel, stainless steal, aluminum, and copper have been carried out at IET, but have not yet been published. Low corrosion rates for steel and aluminum in liquid sodium nitrate can be reported; only coppers seem to corrode in an unacceptable manner. These findings support the above literature based references.

3.5. Heat Transfer Enhancement Methods

The majority of PCMs investigated for use in latent heat TES systems have poor heat conductivities in both the liquid and the solid phase. Only a few materials like metals do not face this challenge, as mentioned above. In the solid phase, the low heat conductivity is the only heat transfer mechanism available and is, therefore, often the bottleneck of the heat transmission from and to the PCM. Various authors have concentrated on heat transfer in PCMs in the past few years, and many enhancement techniques have been tested and evaluated experimentally as well as numerically. Many of these are already discussed in papers, others are accentuated here. A good review on the topic of heat transfer enhancement for PCM is provided by Jegadheeswaran and Pohekar [49] or Ibrahim et al. [45].

Melting and solidification During melting, first conduction and then natural convection occur in liquid PCM. Since heat transfer by conduction is lower than heat transfer by natural convection, conduction becomes almost negligible for the melting process. Due to the volume change, the liquid PCM needs free space to expand into. The influence of natural convection on the melting front has been studied by various authors. Often, the conclusion was that natural convection cannot be neglected for the numerical or analytical modeling of the phase change. Experiments often visually tracked phase change fronts and compared them with calculations like in [87]. For vertically heating surfaces (tubes or walls), the PCM melts and accumulates at the top. Then the melting front evolves with inclination; the upper part melts faster. This behavior was measured during this work and is presented in Paper 1 and Paper 2. In contrast to melting, conduction is the dominating effect for solidification. Interestingly, the solidified layers are

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Fin type	Fin orientation	Tube properties
circle solid membrane square serrated spikes U-fins	longitudinal transversal spiral inside outside	vertical horizontal inclined parallel flow serial flow

Table 3.1.: Fin design criteria

formed parallel to the cooling surface, and they remain in that angle until the PCM is solid. For a comprehensive review, refer to [49].

3.5.1. Extended Heat Exchange Surfaces

Like in any other heat exchanger, the surface corresponds to the power of the heat exchanger. In the HTF-PCM heat exchanger, a larger surface can be reached with the application of fins. Finned tube heat exchangers are standardized components in the energy industry [117] and are applied in boilers, condensers, and many other heat exchanger systems. The tube and the fins are often made of the same material such as finned copper tubes for refrigeration or finned steel tubes for boilers.

A high variety of fins and finned tubes are available, and attention has to be drawn to the orientation of the fins and the tube. In Tab. 3.1 some fin types and orientations for fins and tubes are provided. Theoretically, any combination of fin type and orientation is possible. Common combinations are square fins transversally applied on a horizontal tube [29], or transversal circle fins on vertical tubes as in [19].

With a focus on latent heat TES, experiments and simulations with fins have been carried out by Velraj et al. [118] as early as 1997. For this experiment, the PCM was placed in a tube which had interior fins. With four fins, four PCM chambers are developed, with six fins six chambers respectively. The heating and cooling was performed by positioning the whole PCM tube in a water bath. The water was stirred mechanically so isothermal conditions on the outer side were applied. The results show approximately five times faster solidification with four fins, and for the six finned tube it was even a 30 % faster than the four fins version. Besides the experiments, a phase change formulation was derived and the enthalpy-temperature correlation was modeled with a linear approach. More details are provided in the modeling chapter 4. Arrangements, like the one mentioned from Velraj et al. above, do not have a good HTF to PCM volume ratio; the same happens to the so called triplex tube heat exchanger in [25] from 2017.

For storage applications, the storage material share has to be maximized. Hence the shell and tube design is utilized as follows: The HTF is in the tube and the PCM around. For better heat transfer, fins are attached to the tube. There are a high number of experimental and even more numerical investigations of such TES systems. Johnson describes the novel industrial scale latent heat TES from DLR with an capacity of 1.5 MW h using vertical fins, longitudinally finned [53]. The same arrangement has been tested in lab scale applications, and in a 700 kW h test rig from Laing et al. [66] some years before. Longitudinally finned vertical tubes were applied in the experimental investigations within this work, too. For industrial scale applications, this arrangement seems to be the most promising. When the PCM melts, its density decreases and, therefore, it has to expand. When this expansion is retarded, the pressure in the liquid volume will increase. In order to reduce the risk of high pressure in liquid PCM areas, the vertical tubes stick out of the PCM in the storage tank. The PCM melts first around the tube and can expand in the same moment to the top of the storage. This represents one of the main advantages of this configuration.

Other research studies like Li and Wu [73] compare different PCMs, pure or enhanced with graphite with different HTFs and fin geometries. As an HTF, synthetic oil is often chosen, and molten salt could increase the heat transfer rate as well as composite PCM and extended fin geometries. In his numerical work, Tay et al. concluded that the use of pins instead of fins is not advisable [106].

Other investigated arrangements have been transversal fins (mostly circle or square) on horizontal tubes. Zauner et al. designed a latent heat TES with HTPE acting as storage material [126], and an experimental investigation at University of Lleida, mentioned in Frazzica and Cabeza [29], used the same arrangement. Both of these used rectangular storage containers. Khan and Khan described a paraffin latent heat TES with vertical tube, longitudinally finned in a cylindrical container [56]. The flow through the tubes is serial in contrast to the parallel flow in Johnson et al. [53]. Summing up, there are a lot of design criteria for finned tube latent heat TES. Based on the aforementioned literature, the following design criteria were chosen for the experiments carried out within this work:

- vertical tube
- longitudinal fins
- steel tube
- aluminum fins

The motivation for this combination can be summarized as follows: Vertical tubes longitudinally finned sticking out of the PCM enable the expansion along the tube to the top of the storage. Steel tubes are capable for high pressure of the HTF for direct steam generation. Aluminum shows high heat conduction and seems appropriate for the application. Both aluminum and steel do not show corrosion with pure sodium nitrate. Finally, compared to other enhancement methods, fins are a common and simple solution.

Fin design The fin design, in detail, is related to the fin type. For transversal fins, circles or squares have been used. The latest application of transversal fins is reported by Couvreuret al. [19] in a TES with vertical tubes. For horizontal tubes, Zauner et al. [126] applied squared transversal fins to horizontal tubes. For longitudinal finned tubes,

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Figure 3.9.: Different longitudinal fin designs, 1a from [8], 1b from [51], 2a and 2b from [98], 3a from [95], 3b from [90], 4a and 4b from [86]

the geometry offers a higher degree of freedom. Basis often are star-shaped with four, six, or any other number of fins. More popular have been the arborescent geometries, like those presented in Fig. 3.9. Subfigures 1 and 3 are experimental investigation cross sections while subfigures 2 and 4 are numerically investigated geometries.

The attachment method presented in subfigure 1 was developed at DLR. An arborescent fin geometry divided symmetrically into two parts is fixed with spring steel clips on a steel tube. While in the version 1a the fins are extended with transversal mini-fins, the geometry was further developed for 1b. Johnson applied the version 1b in a cogeneration plant, the manufacturing process of the finned tube with steel clips is described in Johnson et al. [51].

The geometry in subfigure 3 is applied for the experimental investigations at IET. The composition was achieved by using hinge bold clamps presented in 3b. They fix six aluminum profiles, produced by extrusion molding on a steel tube. The assembly using the hinge bold clamps has one significant disadvantage: The cross section can't be hexagonal, and the clamp itself remains on the outside of the cylindrical shape. Hexagonal arrangements of the finned tube would be feasible with space for the hinge bold clamp. For this reason in Paper 3, 4 and 5 the bimetallic tubes have been investigated in detail and a new attachment principle is presented - the bending edge. In Paper 6, 7 and 8 the plain longitudinally finned tube was improved by uniformly adding transversal fins. To be aware of the volume expansion, the transversal fins have a slot between the HTF tube and the fin. The vertical expansion of the PCM is not prevented, but still the melting front is divided into five chambers which increases the heat transfer as described in the aforementioned papers. For the latent heat TES in the present work, an arborescent geometry was chosen like the one presented in 3a.

Subfigure 2 presents the fin geometries chosen by Sciacovelli et al. [98] for his numerical investigation. The more fins applied to the tube, the faster it melted. Interestingly, the chosen tube orientation was horizontal, and the upper half melted obviously faster. In subfigure 4 optimized fin geometries are presented by Pizzolato et al. [86] for horizontal tubes once again. While 4a is optimized for solidification, 4b is the best option for melting. In the large non-finned area natural convection can develop.

Based on the fin geometries presented above, the development of fins is observable. Fin stumps transverse oriented to the fins like extensively used in 1a are no longer used. A potential explanation is presented in [76] based on numerical investigations done at IET. These fin stumps prevent the flow in radial direction during melting, and melting takes longer. In the next step, the attachment solution for bimetallic tubes presented in Paper 3, 4 and 5 has to be tested in experimentally.

3.5.2. Encapsulation

The goal of encapsulation is to completely imbed the liquid PCM in a shell and increase the heat transfer surface. The shell or capsule does not change its phase; it has to be solid over the whole operating temperature range. Another attribute is that they have to manage the volume change of the PCM, which is handled with ullage space in the capsule. The casing is supposed to have high heat conductivity. The performance is reduced by the ullage space filled with e.g. air through the high thermal resistance of air compared to most of the PCMs [27].

Macro-encapsulation For macro-encapsulation a container of any shape is filled with PCM. The container can be either a rectangular box, a sphere, or a tube, etc. . The material used for encapsulation has to be non-corrosive with the PCM and the HTF. During thermal cycling, the PCM is liquid so the sealing may become a problem. Containers could be sealed permanently through welding, brazing, etc. . In the PCM volume, further heat transfer mechanisms can be applied like foams or nanoparticles. For lower temperatures Jegadheeswaran and Pohekar [49] mention many references in their review. For higher temperature applications, Zhang et al. describe the encapsulation of NaNO₃-KNO₃ mixture in tubes with 75 mm outer diameter and a height of 77 mm [128]. Inserted metallic foam and metallic sponge was also tested. The pressure in the container is far below the Young's modulus of the utilized steel AISI 321.

Similar metal capsules but made of aluminum are developed by Höhlein et al. [42], containing the inorganic salt hydrate magnesium-chloride hexahydrate. The aluminum pipes filled with PCM are hermetically sealed. Main drawbacks are current high manufacturing costs due to the mechanical sealing.

Alam et al. [1] developed a technique for encapsulating PCMs, with sodium nitrate beneath them, in the temperature range between 120 °C and 350 °C. The PCM is pressed in spherical shapes, then coated by a polymer. A non-vacuum based technique was then used for coating the metal nickel on the polymer layer. The flexible coating technique allows the use of a very thin but sufficient strength coating. The capsule shows excellent thermal and chemical stability even after 2200 thermal cycles.

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Micro-encapsulation Micro-encapsulation for low temperature levels is frequently reported in literature [27]. The scale for particle diameters of such material is 1 µm to 1000 µm and smaller for nano-PCM particles. While the PCM-shell mass ration is better for macro-scale encapsulation, the micro-encapsulated PCM offer other advantages like the embedding in other materials. For high temperature PCMs, the literature with respect to micro-encapsulation is manageable. Only Zhang describes the process for high temperature PCM so far [129]. Potassium nitrate is coated with a novel water-limited silica coating. It shows excellent stability for > 100 heating/cooling cycles, good controllability of shell formation and high encapsulation ratio of 95.2 %.

Form stable PCMs Shape stabilized PCMs retain their stability over their melting point. The PCM is applied to a carrier material, paraffin is e.g. used for HDPE which creates a solid scaffold in which the paraffin changes the phase without leakage. The PCM retains due to the capillary interaction between the two materials. Different mixing rations and their stability are presented in Fleischer's book [27]. Other approaches for higher temperatures include inorganic salts in high temperature stable carrier materials. Minerals can be used for that purpose, and the characterization of porous minerals is provided in [16]. Vermiculite and carbon graphite seem to be good candidates for solar salt mixtures (NaNO₃/KNO₃) shape stabilized PCM. The vermiculite micro-structure appears to promote stability of the material with sufficient capillary forces for the PCM retain. Graphite improves the heat conductivity of the composition. Cost estimates and further details can be found in [22].

3.5.3. Selected Heat Conductivity/Capacity Enhancements

Besides fins and encapsulation, many other methods are presented in the reviews [49] and [45]. Selected methods should be mentioned in the following short summary. Yanwei et al. measure the specific heat capacities of binary salt and nano-composites [123]. The added particles between zero and two weight percent increased the heat capacity up to 8.3%. The particles added were Al₂O₃ nano-particles, the increased heat capacity is based on a change on Coulomb energy.

Other works, like Tian et al., focus on heat conductivity [107]. A ternary carbonate salt $(Li_2CO_3-Na_2CO_3-K_2CO_3)$ is doped with Mg particles. The melting temperature remained stable while the thermal conductivity could be raised by 45%. As upper working temperature 725 °C are specified under argon atmosphere.

The binary mixture of NaNO₃/KNO₃ was doped with 5%,10% and 15% mass fraction of expanded graphite. The thermal conductivity could be raised to $7 \text{ W m}^{-1} \text{ K}^{-1}$ (compared to $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ for the pure substance) and the composite was used in encapsulated cylinders by Xiao et al. [122]. Many more studies are referenced in the attached papers. The topic of PCM property enhancement is wide, but it is not in the scope of this work.

4. Modeling of Phase Change Phenomena

When designing a latent heat TES, the mathematical description of the phase change is of interest. The description of the melting and the solidification is rather complex and difficult to solve - especially when using complex geometries. A less difficult approach is to describe the storage potential which consists of the individual energy capacities. This global approach is helpful for energy balances of the system - so called system level simulations. In order to do this, the material properties have to be well known. The main properties like the specific heat capacity, the heat conduction, the density, and the latent heat of fusion are all temperature dependent. For some geometries, analytical solutions for the melting and solidification are presented, and finally, numerical modeling with the help of CFD is discussed.

4.1. Modeling of Material Properties

In order to apply proper data analysis to the material properties, mathematical formulations have to be developed for the temperature dependent properties. Referring to Fig. 3.8, the essential properties are related to the temperature. For simple energy balances, the specific heat capacity and the latent heat of fusion are of interest while the other properties, like density and heat conductivity, have to be known for more detailed analytical and numerical modeling.

4.1.1. Heat Capacity and Enthalpy

The foundation for modeling the phase change is formed by expressions for the heat capacity and the enthalpy. In Fig. 4.1, the heat capacity and the enthalpy function are illustrated schematically. Theoretically, the heat capacity function has a peak at the melting temperature and the enthalpy function jumps with the value of the latent heat of fusion. The correlation between the heat capacity and the enthalpy is given as

$$h(T) = \int_{T_i}^{T_f} c_p(T) \, dT \,. \tag{4.1}$$

The heat capacity for pure substances as presented in Fig. 4.1 peaks at the melting temperature. At this temperature the enthalpy shows a step like increase. For mixtures, melting takes place over a temperature range.

4. Modeling of Phase Change Phenomena



Figure 4.1.: Schematic heat capacity and enthalpy functions

Determination of the Enthalpy Function

Based on the measurements of heat capacities and latent heat of fusion e.g. for sodium nitrate in [54], [105] or [17], values for the specific heat capacity are known. For the liquid and the solid range, the heat capacity function can be derived easily with linear or polynomial fits. In many cases, a linear fitting function is sufficient as is presented in Paper 8 [95] for sodium nitrate. In Fig. 4.2, the functions $c_{p,s}(T)$ and $c_{p,l}(T)$ are shown schematically. For the melting range, following assumptions were made:

- A melting range is defined with the solidification temperature T_s and the liquefaction temperature T_l
- The latent heat of fusion L is distributed within the melting range using the equivalent heat capacity function c_p^*
- The heat capacity between T_s and T_l is linearly interpolated with the function $c_{p,m}$
- The equivalent heat capacity function c_p^* is a forth grade polynomial used in Paper 8 (but can be any other function)

The sensible heat $c_{p,sen}(T)$ can be expressed with the sensible heat functions $c_{p,s}(T)$, $c_{p,m}(T)$ and $c_{p,L}(T)$ and is given in Eq. (4.2). For the latent heat of fusion, the equivalent heat capacity function $c_p^*(T)$ is introduced and added to the specific heat in the melting range. The area under $c_p^*(T)$ correlates directly with the latent heat of fusion. Some boundary conditions have to be provided for the functions. They are listed in Paper 8 and are mentioned here again. The equivalent heat capacity function c_p^* is supposed to be zero at T_l and T_s . Furthermore, the first derivative has to correlate with the difference of the first derivative of $c_{p,s}(T)$ and $c_{p,m}(T)$ and $c_{p,l}(T)$ respectively. This ensures continuity at T_l and T_s for the function.

$$c_{p,sen}(T) = \begin{cases} c_{p,s}(T) & T_{lrv} \le T < T_s \\ c_{p,m}(T) & T_s \le T \le T_l \\ c_{p,l}(T) & T_l < T \le T_{urv} \end{cases}$$
(4.2)



Figure 4.2.: Schematic apparent heat capacity function and enthalpy

The heat capacity function as presented in Fig. 4.2 is called apparent specific heat capacity $c_{p,app}(T)$ and comprises both sensible and latent heat of fusion. The function is given in Eq. (4.3). The interesting aspect of this approach is its simplicity as all functions are either linear or polynomial functions which can be easily integrated based on Eq. (4.1) in order to determine the enthalpy function h(T). This enthalpy function represents a direct relation between the measured temperature T and the specific enthalpy of the PCM. With linear or polynomial c_p functions, the enthalpy will also be a linear or polynomial function and, therefore, is fast and easy to apply to any model.

$$c_{p,app}(T) = \begin{cases} c_{p,s}(T) & T_{lrv} \le T < T_s \\ c_{p,m}(T) + c_p^*(T) & T_s \le T \le T_l \\ c_{p,l}(T) & T_l < T \le T_{urv} \end{cases}$$
(4.3)

Selected Approaches

The distribution of the latent heat of fusion can be done by any arbitrary function. In the work from Velraj et al. [118], a simple linear function is applied. Other authors like Rösler and Brüggemann [92] use an error function for this purpose, applied to the liquid fraction γ . The error function is compared to a linear function in the mentioned literature. A comparison with the polynomial approach is done in Paper 8. The foundation for the chosen method is provided by Cao and Faghri [15]. They introduced the equivalent heat capacity, melting takes place over a specific temperature range and provides enthalpy functions.

One of the issues using this material property description may be the question of how to chose T_s and T_l , as it depends on the considered volume size and heating rates. The larger the considered volume, the larger the temperature spread will be. Similarly higher heating rates will also cause the temperature spread to be larger. It would be interesting to investigate the accuracy for different spreads. For application in the experimental analysis of the latent heat TES in Paper 6, Paper 7 and Paper 8 with a radial discretization of four sections, a temperature spread of \pm 6 °C for sodium



Figure 4.3.: Stefan problem with solidification from left to right

nitrate was chosen.

Another aspect is the choice of the enthalpy zero. Due to the fact that enthalpy differences are of interest and not absolute enthalpies, the choice could be random. For the enthalpy function in Paper 8 0° C was chosen with lower and upper temperature range values of 0° C and 400° C.

4.2. Analytical Models

Analytical solutions of the so called Stefan problem are available only for simplified models with various assumptions. The Stefan problem is a boundary value problem for a partial differential equation which aims to describe the temperature distribution in a homogeneous medium undergoing a phase change. The Stefan condition describes a surface between the liquid and the solid phase which is unknown and drives from the solid to the liquid end in the 1-D case, like described by Fleischer in [27] and presented in Fig. 4.3.

The heat equation in one dimension for the solid region is provided in Eq. (4.4) and for the liquid region in Eq. (4.5). The thermal diffusivity a can be assumed to be constant for this specific purpose.

$$\frac{\partial T_s}{\partial t} = a_s \frac{\partial^2 T_s}{\partial x^2} \qquad t > 0, 0 < x < X(t) \tag{4.4}$$

$$\frac{\partial T_l}{\partial t} = a_l \frac{\partial^2 T_l}{\partial x^2} \qquad t > 0, X(t) < x \tag{4.5}$$

At the interface X(t) the Stefan condition is applied (Eq. (4.6)). These and the other required conditions are given in the following equations. The Stefan condition is needed to obtain closure of the PDE. Other conditions like (Eq. (4.7)) describe the temperature on the left side T_b . Eq. (4.8) describes the Dirichlet condition at the melting front with the constant melting temperature. Eq. (4.9) is the initial temperature distribution along x at the starting time and Eq. (4.10) is the initial melting front position.

$$L \rho \frac{\partial X}{\partial t} = \lambda_s \frac{\partial T_s}{\partial x} - \lambda_l \frac{\partial T_l}{\partial x} \qquad t > 0, x = X(t)$$
(4.6)

$$T_s(0,t) = T_b \qquad T_b < T_m \tag{4.7}$$

$$T(X(t),t) = T_m \qquad t > 0 \tag{4.8}$$

$$T(x,0) = T_i \qquad x > 0$$
 (4.9)

$$X(0) = 0 (4.10)$$

The dimensionless Stefan number St is provided in Eq. (4.11) and is related to the rate of melting or solidification in a semi-infinite region. T_b is the temperature at the boundary and the temperature difference to the melting point correlates to the so called driving temperature spread.

$$St = \frac{c_p \left(T_b - T_{melt}\right)}{L} \qquad t > 0 \tag{4.11}$$

The solution of the Stefan problem in this simplified version can be achieved with similarity methods, applying the similarity variable η given in Eq. (4.12).

$$\eta = \frac{x}{2\sqrt{a_l}} \tag{4.12}$$

The Neumann's solution for the interface can be written as follows. k_N represents the dimensionless number in solution of Neumann's problem:

$$X(t) = 2k_N\sqrt{a_l t} \tag{4.13}$$

The number k_N can be derived from the transcendental equation for a given St number from:

$$k_N e^{k_N^2} \operatorname{erf}(k_N) = St/\pi \tag{4.14}$$

The temperature in the solid phase can be written finally:

$$T(x,t) = T_b + (T_m - T_b) \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{a_s t}}\right)}{\operatorname{erf}\left(\frac{X(t)}{2\sqrt{a_s t}}\right)}$$
(4.15)

Applying Fourier's law, the heat flux can be written as:

$$f = \frac{\lambda \left(T_m - T_b\right)}{\sqrt{\pi a} \operatorname{erf}(k_N)} t^{-0.5}$$
(4.16)

As can be seen from equation (4.16), the heat flux decreases with the time due to the increasing thermal resistance between the melting front X(t) and the left side. This transient behavior and the need to enhance heat transfer abilities have been discussed in the previous chapter. The mathematical foundation for the enhancement necessities

4. Modeling of Phase Change Phenomena

is presented here.

The two-phase Stefan problem in one dimension can found here: [43]. For cylindrical coordinates they present an exact solution using an exponential integral function. The heat source is a line, the melting front moves in radial direction. Assumptions are made as before with constant thermophysical material properties. Exact analytical solutions only exist for semi-infinite problems with constant parameters in each phase and constant initial and boundary temperatures. For the case of constant heat flux, no exact analytical solution exists. Clearly then, for a realistic case, one is forced to apply approximate solutions or numerical approaches.

4.2.1. Approximate Analytical Solutions

Referring to the simplest Stefan problem, the boundary condition of steady heat flux on one side is a problem for which no analytical solution exists. Hu and Argyropoulos [43] describe approximate solutions based on integral equations expressing the overall heat balance of the system by integrating the one-dimensional heat conduction equation with respect to the spatial variable x and inserting boundary conditions. The method was used to solve single-phase melting-ice problems with various boundary conditions like constant heat flux. The heat balance integral method was applied to different problems with the intention of easing and improving mathematical analysis.

Lamberg and Sirén [68] present a simplified, one-dimensional, analytical model based on a quasi-linear, transient, thin-fin equation. The geometry is a two-dimensional PCM storage with internal fins for which no analytical solution had been found, but it is simply solved by numerical methods. The solutions are compared in order to determine the accuracy of the approximate analytical solution. A high number of assumptions are made for this purpose, such as equal initial temperature, one dimensional temperature distribution in the fin, two regions with one-dimensional heat transfer in x-direction and y-direction respectively, neglected sensible heat in one region, and constant thermophysical properties of the PCM. Lamberg and Sirén compared different fin materials and PCMs and the one-dimensional analytical and numerical model with the two dimensional numerical model. In addition, they introduce the liquid fraction γ . The conclusions drawn by the authors can be summarized as follows:

- The geometry of the computational domain is one of the most important factors.
- The accuracy of the analytical solutions is good; the assumptions made to enable analytical solutions have minor influence.
- The assumptions made for simplifying the two-dimensional model affect the accuracy more than the assumptions made for solving the one-dimensional model analytically.

A different approach is presented by Bauer [7] referring to the high number of required equations in the approximate analytical solution from Lamberg and Sirén. Bauer chooses a plain wall geometry with fins with isothermal heat extraction at the wall and the thickness of zero. The other walls are considered adiabatic, symmetry conditions are applied. The approximation is that the fins and the PCM can be considered as a single material with effective properties. The dimensionless fin factor ϵ is created, and the one dimensional steady state heat flow ratio compares the heat flow in the fin with the heat flow in the PCM. These factors are applied and results are provided for the plain wall with fins and the finned tube with transversal fins. The volume averaging method is a useful approach for heat conduction problems in thermal equilibrium.

4.3. Numerical Approaches for Melting

Basically any numerical method can be applied to model phase change problems. This includes finite differences, finite-elements, and finite-volume methods. Many numerical simulations are carried out with the help of commercial and non-commercial software tools. Reviews on the modeling of phase change phenomena are provided by Dutil et al. [24], Verma et al. [119] and Hu and Argyropoulos [43] with different perspectives. Models calculating the exact position of the melting front as function of time and space are called strong formulations, while applying one set of equations to the whole domain is discussed as weak formulation. Numerical descriptions of the phase change phenomena consider the phase change and heat conduction as well as convection/diffusion depending on the complexity of the model. Volume changes are often neglected because they have little influence on heat transfer. The dependence of the material properties on the temperature can be directly implemented for weak formulations. Convection in the PCM can play a role for low-viscosity PCM and influence the heat transfer significantly. Boussinesq approximations for laminar flows can be applied for treating the convective flow. Other effects like hysteresis of enthalpy/temperature are not considered as well as subcooling in many of the mentioned numerical analysis.

Fixed grid or adaptive mesh The discretization of geometries for numerical modeling can be either done by the use of fixed grids or so called adaptive meshes. Regarding the phase change phenomena, the challenge is to estimate the melting front position within the grid. For fixed grids, the melting front is situated between two adjacent points. In order to increase accuracy, the grid should be fine. A different approach is the adaptive mesh method in which the grid density increases around the melting front. The difficulty in this is to maintain the data structure since the topology and the of grid points have to be determined for each time step [24].

4.3.1. Enthalpy and Apparent Heat Capacity

The main advantage of the weak formulation is based on the fact that only one set of equations is necessary to describe the whole domain. The phase change itself is considered as a material property (apparent heat capacity) or as part of the enthalpy function. The apparent heat capacity method is basically adding the latent heat of fusion to the sensible heat. Then, the apparent heat capacity can be used in the one dimensional heat conduction equation of e.g. this form:

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$$\rho c_{p,app} \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right)$$
(4.17)

This equation can easily be discretized and solved numerically. Several authors applied this method with finite difference formulation for one- or two-dimensional problems. Problems can occur through the punctual consideration of the latent heat which can lead to singularities and require small time steps as described in [43]. In order to overcome this drawback, the latent heat has to be distributed to a temperature range which is not formally valid for pure substances. This distribution can be either linear [118] or any other probability distribution such as Normal, Gumbel, Weibul or Lognormal distribution [4]. The distribution has to fit the measured heat capacity values, and this process is described in Paper 8.

The enthalpy method is comparable to the apparent heat capacity method. Instead of calculating with heat capacities, the equations are enthalpy based. The correlation is provided in Eq. (4.1). The enthalpy can be applied either at one temperature, resulting in a discontinuous function for the enthalpy, or distributed over a specific temperature range. The integration of the apparent heat capacity is simple for simple formulations, as demonstrated in Paper 8 regarding polynomial distribution of the latent heat of fusion.

4.3.2. Convection and Diffusion

For solving convective heat transport in the liquid phase, the buoyancy forces can be considered with Navier-Stokes equations. The convection has a significant influence on the melting behavior and can not be neglected in comprehensive numerical analysis of phase change problems. The mass, momentum, and energy Navier-Stokes equations have to be solved, due to their non-linearity, the solution is normally achieved by numerical methods; analytical solution are available only for a few simple examples [43].

4.3.3. Selected Models

A rough overview of the individual mathematical formulations of the past few decades are presented here without making the claim of being complete. In 1978, Solomon [102] proposed a weak solution and the enthalpy method for different geometries concluding that natural convection cannot be neglected. Zonquin and Bejan [130] investigated solidification within their work, suggesting a solid subcooling parameter to better describe the process. Evaluation with experiments are presented and good agreement of the theoretical model has been achieved. In 1989 Hirata and Nishida [39] calculated the natural convection heat transfer in an isothermal cylinder. They demonstrated the effect of natural convection and applied an equivalent thermal conductivity. Cao and Faghri [15] concluded that the lateral conduction heat transfer rate can have a significant effect on the melting velocity.

A finite element shell and tube model was presented by Gong and Mujumdar [33]. The model was limited to only conduction controlled melting and freezing and compared



Figure 4.4.: Contours of the PCM liquid fraction at different time from a) [120], b) and c) from [57]

to different operation modes of the shell and tube system. Differences appear when charging and discharging happens not from the same HTF direction.

In the past few years the so called Lattice Boltzmann method was applied for many different problems including phase change such as Li et al. described in [72] and [70]. A review of the application of Lattice Bolzmans methods for single and solid-liquid phase change materials was provided by He et al. [37]. Conduction and convection are taken into account and two-dimensional solutions are compared to analytical conduction controlled results, and validation of the methods was presented. The two-dimensional model was then extended to a three-dimensional model in 2017 [69].

Heydari and Talati [38] presented the application of the Tau method for phase change problems. They concluded that the storage dimension has a significant impact on the melting front position, and the cell aspect ratio effects the heat transfer. The Tau method can be regarded as a simple approach with good performance.

Finite difference schemes and reduced models are still useful for modeling whole storage systems like Barz et al. proposed [4]. System level models are necessary for comparison and implementation of TES to energy systems. A two-dimensional shell and tube model has been validated and included detailed information about the storage system. A nonlinear state observer was designed for reconstructing the transient spatial temperature field in the TES by Barz et al. [5]. The observation was validated with a lab-scale test rig, and it robustly tracked the real process data with only four internal PCM temperature sensors. Part load conditions were modeled by Parhizi and Jain in their work [85] for melting of a PCM.

Three-dimensional modeling for a section of a latent heat TES with finned heat pipes was presented by Tiari and Qiu [108]. They used the enthalpy porosity method to simulate the phase change. Heat pipes can play a crucial role in increasing the heat transfer rate. The modeled natural convection significantly increased the heat transfer rate.

Kuboth et al. [62] tried to increase the fin density at the end of a finned tube heat

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exchanger and compared the results to uniformly distributed transversal fins. Numerical results indicated a change of only 3% and, therefore, little enhancement.

The topic of multiple phase change materials filled into capsules was modeled in [71]. Depending on the PCM type and the position in the storage, the performance can be adjusted.

Focusing on different enhancement methods, Koller et al. [57] concluded that longitudinal fins are preferable to transversal fins due to the faster melting. He compared transversal, longitudinal fins and wired frame, the two first mentioned are shown in Fig. 4.4 b) and c). Although the wired frame design showed the highest power rate for charging, the fin design showed more constant power rates. Longitudinal arborescent fins were compared to each other with small lateral fins in between by Walter et al. [120]. This fin type (with lateral fin) is used for the experimental investigation presented in the following papers. The small lateral fin hinders the PCM convection and therefore reduces the heat transfer rate as is presented in Fig. 4.4 a). For the assembly of the finned tube in the papers, the hinge bold clamp fixes the six fin-parts on the steel tube (Fig. 3.9). The lateral fins were applied intending to increase mechanical stability. Applying a fin design with bending ears as presented in Paper 3, Paper 4 and Paper 5 would make the hinge bold clamp needless and therefore the lateral fins, too.

4.4. System-Level Simulations

While numerical solutions are available for small geometries and numerical domains due to computational effort, especially for three-dimensional models, system level simulations require fast and reliable storage behavior descriptions. For this purpose, reduced PCM storage models like in Barz et al. [4] are needed.

For other TES systems, like sensible molten salt storage with filler material, reduced models are available in papers such as [28]. Flueckinger et al. modeled a 100 MW solar thermal plant with thermocline molten salt storage tank and was able to significantly increase the capacity factor.

For phase change materials, la Calle et al. [64] presented the viability and the annual performance of a solar plant with latent heat TES and supercritical CO_2 power block. The simulation suggested that the system was viable and reduced the LCOE. The over-all concept is presented in Fig. 4.5.

4.4. System-Level Simulations



Figure 4.5.: Schematic concept of the system level simulation of the Na - PCM - $\rm sCO_2$ plant from [64]

5. Experimental Investigations

Two latent heat TES test rigs were designed and built for the experimental investigations. In addition to the test rigs, experiments with bimetallic finned tubes were also completed. This work is concisely outlined in this chapter, and similar works from other research institutions are presented. This allows a classification of the experiments and provides a good overview of the experimental research in this field, without claiming to be complete.

5.1. Latent Heat TES Test Rigs

For the experimental investigations carried out within this thesis, two test rigs were built, one in 2013 and another one in 2018. Both rigs consisted of a shell and tube heat exchanger with a finned mono tube, vertically arranged. The main differences between the two rigs exists in the fin geometry and in the higher number of temperature testing points of the newest test rig. The results are presented in Paper 2 and 2 and Paper 6, 7 and 8 respectively. The mono tube composition was chosen after constructing a latent heat TES system with seven vertically finned tubes with serial HTF flow [90] in order to determine a more detailed melting behavior. With serial flow through seven vertical tubes, the melting front cannot be detected accurately enough. The same longitudinal fin geometry used by Prötsch [90] is used for both test rigs.

A thermal oil plant with the HTF Therminol VP1[®] is used as a heat source and sink, HTF inlet flow temperatures of up to 400 °C are possible and a mass flow of 3 kg s⁻¹ can be established. Therminol VP1[®] is a mixture of biphenyl and diphenyl oxide and is a clear liquid. It solidifies at 12 °C, hence the whole surrounding piping is supplied with trace heating systems. The thermophysical properties are provided by the manufacturer [103]. The vapor pressure at 400 °C is about 10.90 bar, a nitrogen overlay is established with a maximum pressure of 16 bar. The whole system was built using the pressure equipment directive, and was approved by a notified body. The control of the thermal oil plant was integrated in a process control system (PCS) called APROL from B&R Industrial Automation GmbH. The PCS was programmed and configured at IET. For the latent heat TES test rig, automatic operations were developed whereby the whole charging and discharging cycles were retraced automatically.

For the experimental investigations, cycle parameters were defined in order to compare the different geometries and measurements with each other. Charging and discharging times vary as well as temperature spreads between the HTF inlet and the melting temperature. Furthermore, the HTF mass flow was part of the investigation. While in Paper 1 and 2 the main aims were the issue of the flow direction of the HTF and the melting behavior, in Paper 6 to 8 the new fin geometry was the main focus. The

5.2. Bimetallic Finned Tube Investigation



Figure 5.1.: Test rig of the mono-finned tube latent heat TES uninsulated (a), the novel combination of fins (b) and the fins fixed with hinge bold clamps (c) and (d)

longitudinal fins remained the same, but they were interrupted by transversal fins at uniform distances. This combination of transversal and longitudinal fins had not been part of experimental investigations at time of publication, to the best knowledge of the author.

The temperature in the HTF and the PCM was logged and later evaluated using MATLAB in Paper 8, the heat transfer was investigated in detail. Therefore, the apparent heat capacity or enthalpy method was applied as described above. The test rigs are presented in Fig. 5.1.

5.2. Bimetallic Finned Tube Investigation

The heat transfer enhancement with fins begs the question of how to attach the aluminum fins onto a steel tube. Aluminum is preferred because of its high heat conductivity and the steel tube was chosen for its high strength and pressure resistance. Different attachment methods are investigated and evaluated in Paper 3, 4 and 5.

For this bimetallic finned tubes, the strength of the combination has to be guaranteed over the whole operation's temperature range and lifetime - from surrounding

5. Experimental Investigations



Figure 5.2.: Prototypes for bimetallic finned tubes (a) and assembly apparatus with assembled tube (b) and (c)

temperature up to $350 \,^{\circ}$ C for years. A cycling thermal load is applied to the composition while charging and discharging. Since the composition is in direct contact to the PCM, corrosion has to be avoided. Finally, the whole composition has to be easy to manufacture and assemble.

Another crucial aspect regarding the bimetallic finned tube is the different heat expansion coefficient of steel and aluminum. The thermal expansion of aluminum is twice as high as the thermal expansion of steel; this would lead to a gap when steel and aluminum fins are manufactured with the same diameter at room-temperature.

Four different prototypes were tested like shown in Fig. 5.2 a). All prototypes had a difference in diameter in order to overcome the thermal expansion problem. Thus, the manufacturing was more challenging. One prototype with a so called bending ear could be spread and the ear would undergo elastic deformation during assembly. The other prototype - a classical press fit - was assembled by pressing the steel tube onto an aluminum tube. Prototype three had a zinc layer in between the steel and the aluminum, and prototype four was a press fit with transversal fins. All prototypes were part of finite element analysis before testing them in experiments. The prototypes were then manufactured and tested in a muffle furnace and a material testing machine. Using the material testing machine, the holding force of the composition was determined at surrounding temperature and operation temperature. The measurements were repeated at the beginning and after 260 cycles in the furnace. The only promising prototype was the so called bending ear. For this prototype, an assembly apparatus was constructed (Fig 5.2 b)) and a small prototype with simplified fins (Fig 5.2 c)) was assembled and tested in the muffle furnace once again. The bending ear concept seemed to be promising. The next step should be testing it in a latent heat TES test rig under real storage conditions.

5.3. Selected Experimental Investigations

For allocating the experimental investigations carried out within this work, the neighboring experimental work should be highlighted. In short, the temperature range of more than 300 °C reduces the quantity of available experiments and also the specific application as TES; the chosen heat transfer mechanism (fins) does the same. Not more than a handful of experimental projects of this TES type can be found in the past ten years. Three of the selected projects are presented here. Among them, the DLR in Germany has developed many industrial scale prototypes of TES in general, but also latent heat TES in particular. At Ghent University and the AIT, two smaller prototypes were built. These are included in the attempt of drawing a more comprehensive picture of the experiments.

5.3.1. Experimental Work at DLR

At DLR, many different PCM test rigs have been erected within the past 15 years. The experimental work focuses mainly on high temperature storage systems for CSP plants and industrial applications. The PCM storage is mostly used as vaporizer in the steam generation process, preheater and superheater could be sensible storage systems, like Laing et al. present [67]. The storage is discharged in natural circulation mode and charged with forced circulation in the other direction. Before erecting a 700 kW h prototype, a lab scale 15 kW h test rig is tested in the lab. Sodium nitrate serves as PCM for both systems, aluminum fins attached onto the steel tubes are used to increase the heat transfer rate into the PCM. Laing et al. present further results of this storage unit [66]. The direct steam generation (DSG) from a PCM storage is feasible for all three operational modes (once-through, natural circulation and forced-circulation), and the concept is presented in Fig 5.3. In addition, a new fin geometry for longitudinal fins is developed and tested in a lab scale storage. The development of the fins, especially the attachment of the aluminum fins on the steel tube, is discussed by Johnson et al. [52]. A new method is proposed: the use of spring steel clips to fix two symmetric aluminum fin halves on the steel tube. The attachment of aluminum fins on a steel tube is also the main focus of Paper 5.

Based on the concept of a high power level TES by Johnson et al. [53], [50], these finned tubes are applied to a co-generation power plant [51]. A heat and power cogeneration plant with a gas turbine and a heat recovery steam generator, which also has a backup boiler, is equipped with a latent heat TES. For the case of tripping the gas turbine, the backup boiler, responsible for constant steam production, is supplemented by the latent heat TES in order to reduce the operational hours of the backup boiler. The latent heat TES is designed for a high power rate of up to 6 MW and with a capacity of 1.5 MW h which would supplement the backup boiler for approximately 15 min. Only simulation results have been published so far, but experimental data is expected soon. Pictures of the finned tube and the storage system are displayed in Fig. 5.4.

5. Experimental Investigations



Figure 5.3.: Schematic set-up of the PCM storage in a water/steam loop with circulation cycle is shown. Discharging mode (left) shows the piping used in black/black-and-white for natural circulation and dashed/black-and-white for forced circulation; charging is shown on the right in once-through operation with black-and-white piping denoting used piping from [66]



Figure 5.4.: PCM storage application in the plant (a) and assembled finned tubes from [51]

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5.3.2. Experimental Work at Ghent University

The application of organic Rankine cycles to utilize low temperature waste heat and increase the energy efficiency of energy intensive industries is often restrained by volatile availability of the waste heat. In the experimental investigations at Ghent University, Couvreur et al. demonstrate the use of a latent heat TES to ensure constant inlet temperature to an ORC cycle [18]. The experimental setup consists of a storage vessel with vertical transversal finned tubes, filled with 2 m^3 solar salt, a eutectic mixture of sodium nitrate and potassium nitrate (Fig. 5.5 a) and b)). Thermal oil (Therminol 66) is used as HTF between the electrical heater, the storage and the ORC process. The storage capacity of 112 kW h is based on the phase transition enthalpy and 220 kW h including the sensible enthalpy between 180 °C and 250 °C. The TES system unit itself is discussed by Couver et al. [19] and further tests are presented in the mentioned literature. The dependency of the power rate from HTF mass flow is documented as well as an approach to determine a global heat transfer coefficient from the HTF into the storage material.

The comparison of these values with experimental investigations at TU Wien is of interest due to the comparability of the storage systems in terms of similar PCMs, temperature levels, and sizes. The overall heat transfer coefficient k (named U in the mentioned literature) reaches values between $150 \,\mathrm{W m^{-2} K}$ and $300 \,\mathrm{W m^{-2} K}$ which corresponds to values measured at TU Wien which are between $260 \,\mathrm{W m^{-2} K}$ and $300 \,\mathrm{W m^{-2} K}$ with different fin geometry and pure sodium nitrate.

A more detailed look on the melting of PCM is presented by Plas et al. [87] based on his master's thesis [88]. An experimental analysis of RT35HC in an rectangular enclosure is presented and liquid fraction functions are experimentally determined. The melting is axially non-uniform, the liquid fraction accumulates at the top of the storage, and the melting front grows from the inside out and from the top to the bottom. For high temperature materials like sodium nitrate, this effect was also demonstrated at TU Wien and presented in Paper 1; although, the melting front cannot be visually measured at this temperature level.



Figure 5.5.: Picture of the installed LHTES unit in Ghent (a) and cross sectional view (b) from from [19], latent heat TES with transversal fins and HDPE as PCM at AIT from [126] (c) and tube bundle with PCM filled tube from [127] (d)

5.3.3. Experimental Work at AIT

At AIT, different polymers have been the focus for their utilization in a latent heat TES. Zauner et al. describes the selection process of HDPE as storage material and the construction of a latent heat TES labor scale test rig in [126]. Heat transfer characteristics of the experiments are provided and compared to numerical simulations. The general aim is to reduce CO_2 emissions in district heating networks or similar applications by using a latent heat TES. The storage design consists of horizontal tubes with transversal fins in a rectangular enclosure (like shown in Fig. 5.5c), and thermal oils serve as HTF. The temperature level is lower compared to sodium nitrate, the HDPE melts around 120 °C. The resulting experimental data are used for validation of a model developed by Barz et al. [4]. The model is supposed to be applied at system-level simulation and therefore has to be reduced compared to full CFD simulations.

Further development led to a hybrid TES consisting of tubes filled with HDPE arranged vertically in a shell and tube heat exchanger with an HTF flow around the tubes [127]. The tubes filled with 208 kg HDPE surrounded by 515 kg of thermal oil form the bundle as it is shown in Fig. 5.5 d). The power rate can be increased by decreasing the tube diameter and increasing the number of tubes. Using larger diameters, the

sensible storage capacity increases, just as Zauner et al. explain. A possible application is also given in [125]. In pulp and paper production, excess steam is often condensed in an auxiliary condenser. Instead, the steam could be used for charging a latent heat TES thereby increasing the utilization of the heat. A small prototype and a storage model are presented for this specific purpose.

6. Conclusion and Outlook

Several improvements of latent heat TES systems have been developed and experimentally investigated during the completion of this work. The most important findings are summarized at this point. The outlook of resultant research topics and ideas is discussed to draw a rough pathway for future research projects.

Experimental work First, a prototype latent heat TES with sodium nitrate and aluminum fins was designed and built. The capacity, the power rate and the energy density could be determined successfully. The melting behavior was described based on temperature plots and the influence of the heat transfer fluid flow direction was investigated for a finned vertical tube arrangement.

Then, the attachment of aluminum fins on a steel tube was investigated experimentally. Using hinge bold clamps works fine, the optimal spatial arrangement of hexagonal cross section bimetallic tubes is not feasible with them. A novel fin geometry with implemented attachment mechanism, the so called bending ear, was designed and tested at operation temperature.

For the second prototype of a latent heat TES, a novel arrangement of different fin types was applied in order to improve the heat transfer rate. The plain longitudinal fins from the first prototype were changed to a novel combination of longitudinal and transversal fins. Again, the main storage parameters were determined and compared to the previous fin design.

Highlights In latent heat TES with plain longitudinal vertically finned tubes, the melting occurs axial asymmetrically. The liquid storage material expands to and accumulates at the top of the storage vessel. Furthermore, there is a slight influence of the flow direction of the heat transfer fluid. Charging with the hot heat transfer fluid from the top leads to shorter melting cycles, which is not observed for discharging cycles.

Connecting aluminum fins on a steel tube without additional components was realized successfully. The bending ear geometry - implemented in the extrusion molding profile geometry of the fins - allows an assembling at room temperature and ensures a press-fit connection also at operational temperature. Hexagonal or any other cross sections are technically feasibly with the new design, the spatial arrangement is not affected by clamps. The connection was tested successfully for creeping at operational temperature. A prototype assembling apparatus was designed and tested for the finned tube production.

The experiments with the combination of two fin types - transversal and longitudinal fins - showed significantly higher melting rates than the plain longitudinally finned rig.

The melting is axially symmetric for the second prototype latent heat TES. With the help of this prototype, an apparent heat transfer coefficient for sodium nitrate latent heat TES with aluminum fins and its dependence on the charging state was determined. With these values and the other identified storage parameters, the behavior and especially the power rate of similar systems can be estimated.

Reflection and Outlook Referring to the implementation barriers (IB2 heat transfer enhancement and IB3 dynamic behavior) for the latent heat TES technology, significant advances were reached for the heat transfer rate with the novel fin combination. The asymmetric melting was demonstrated and the influence of the flow direction was shown. The dynamic behavior of this TES types was measured and can be used to develop control strategies. For upscaling (IB5), the measured heat transfer values allow power and capacity estimations for large scale systems. Finally, the data is available for validation of mathematical TES models of this TES type.

For future research projects, an interesting research questions could be the design of such a storage system in general. For this purpose the prediction of the heat transfer coefficient and hence the expectable power rate are a determining factor. This is challenging if there are no measured values or correlations available. A general relation between the fin type, the storage material and the phase state for calculating the heat transfer rate should be developed.

From an application perspective, the power rate is of high interest as mentioned before. But for this purpose the phase state has to be known. A relevant research question may be how to determine the phase state/state-of-charge of non-lab scale latent heat TES applications based on few temperature testing points?

Latent heat TES systems show a highly transient behavior. For the use in energy systems, control strategies have to be developed for a successful operation. This will mainly effect the mass flow of the heat transfer fluid. When used as vaporizer in a steam generating systems, the latent heat TES may work with natural circulation. Controlled charging and discharging is important for the successful implementation in energy systems.

The next step, from a technological point of view, is testing a storage system under real conditions in the field. This could be either in a CSP plant or any waste heat facility. For higher capacities and power rates, a high number of tubes is necessary. Then, the question of tubing appears. How many collector tubes at the bottom and the top supply the heat transfer tubes and how high is the pressure loss of the individual tubes? Especially when the latent heat TES is used as vaporizer/condenser in a steam generator, the issue of stable flow conditions in the individual tube appears.

The bimetallic finned tube with bending ear geometry has to be tested in manufacturing, assembly and under real conditions in the storage systems in order to gain more experience with this technology. Based on the actual work the tolerances for extrusion molding may be crucial for a successful implementation of this technology.

For the application of latent heat TES models in simulations on system level scale, the behavior of the latent heat TES has to be considered or controlled, as mentioned

6. Conclusion and Outlook

above. Then, models of latent heat TES systems have to be developed for the different simulation software packages available. The mentioned research topics are essential to raise the technology readiness level of latent heat TES systems for their application in future energy systems.

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A. List of Publications

Paper 1

Georg Urschitz, Heimo Walter, and Michael Hameter. "Experimental Investigation of a Finned Mono Tube - Latent Heat Thermal Energy Storage (LHTES)". in: *Proceedings of* the ASME 2014 8th International Conference on Energy Sustainability. Ed. by ASME. 2014

Paper 2

Georg Urschitz, Heimo Walter, and Michael Hameter. "Laboratory Test Rig of a LHTES (Latent Heat Thermal Energy Storage): Construction and First Experimental Results". In: Journal of Energy and Power Engineering 8 (2014), pp. 1838–1847

Paper 3

Georg Urschitz et al. "New Design of a Bimetallic Finned Tube for the Use in Latent Heat Thermal Energy Storage Units". In: *Proceedings of the ASME 2015 9th International Conference on Energy Sustainability.* Ed. by ASME. 2015

Paper 4

Georg Urschitz, Heimo Walter, and Jens Brier. "Experimental Investigation on Compositions and Materials for Finned Bimetal Tubes for the use in Latent Heat Thermal Energy Storage Units". In: *Proceedings of the 10th Conference on Sustainable Development of Energy, Water and Environment Systems - SDEWES 2015.* Ed. by University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture. 2015

Paper 5

G. Urschitz, H. Walter, and J. Brier. "Experimental Investigation on Bimetallic Tube Compositions for the Use in Latent Heat Thermal Energy Storage Units". In: *Energy Conversion and Management* 125 (2016), pp. 368–378. ISSN: 01968904. DOI: 10.1016/ j.enconman.2016.05.054

Paper 6

Georg Scharinger-Urschitz et al. "Experimental Investigation on a High Temperature Latent TES with Novel Fin Geometry". In: *Proceeding of the 13th Conference on Sustainable Development of Energy, Water and Environment System - SDEWES 2018.* Ed. by University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture. 2018. ISBN: 1847-7178

Paper 7

Georg Scharinger-Urschitz, Heimo Walter, and Thomas Bauernfeind. "Novel Fin Geometry for a Latent High Temperature Thermal Energy Storage - Experimental Investigation". In: *Proceedings of the 4th Thermal and Fluids Engineering Conference (TFEC 2019)*. Ed. by ASTFE Digital Library. 2019, Paper Number 27516. ISBN: 978-1-56700-472-4

Paper 8

Georg Scharinger-Urschitz, Heimo Walter, and Markus Haider. "Heat Transfer in Latent High-Temperature Thermal Energy Storage Systems—Experimental Investigation". In: *Energies* 12.7 (2019), p. 1264. ISSN: 1996-1073. DOI: 10.3390/en12071264

A.1. Paper 1

Georg Urschitz, Heimo Walter and Michael Hameter

Experimental Investigation of a Finned Mono Tube - Latent Heat Thermal Energy storage (LHTES)

Proceedings of the ASME 2014 8th International Conference on Energy Sustainability

A.2. Paper 2

Georg Urschitz, Heimo Walter and Michael Hameter

Laboratory Test Rig of a LHTES (Latent Heat Thermal Energy Storage): Construction and First Experimental Results

Journal of Energy and Power Engineering 8 (2014), pp. 1838-1847

A.3. Paper 3

Georg Urschitz, Jens Brier, Heimo Walter, et al.

New Design of a Bimetallic Finned Tube for the Use in Latent Heat Thermal Energy Storage Units

Proceedings of the ASME 2015 9th International Conference on Energy Sustainability

A.4. Paper 4

Georg Urschitz, Heimo Walter and Jens Brier

Experimental Investigation on Compositions and Materials for Finned Bimetal Tubes for the Use in Latent Heat Thermal Energy Storage Units

Proceedings of the 10th Conference on Sustainable Development of Energy, Water and Environment Systems 2015

A.5. Paper 5

Georg Urschitz, Heimo Walter and Jens Brier

Experimental Investigation on Bimetallic Tube Compositions for the Use in Latent Heat Thermal Energy Storage Units

Energy Conversion and Management 125 (2016), pp. 368–378

A.6. Paper 6

Georg Scharinger-Urschitz, Michael Hameter, Viktoria Illýes, et al.

Experimental Investigation on a High Temperature Latent TES with Novel Fin Geometry

Proceedings of the 13th Conference on Sustainable Development of Energy, Water and Environment System 2018

A.7. Paper 7

Georg Scharinger-Urschitz, Heimo Walter and Thomas Bauernfeind

Novel Fin Geometry for a Latent High Temperature Thermal Energy Storage - Experimental Investigation

Proceedings of the 4th Thermal and Fluids Engineering Conference ASTFE 2019

A.8. Paper 8

Georg Scharinger-Urschitz, Heimo Walter and Markus Haider

Heat Transfer in Latent High-Temperature Thermal Energy Storage Systems - Experimental Investigation

Energies 2019, 12, 1264

Georg Scharinger-Urschitz

Curriculum Vitae

	Professional experience
11/2015–present	 University assistant, <i>TU Wien</i>, Vienna. At the Institute for Energy System and Thermodynamics Research on thermal energy storage systems Design, set-up and management of various test-rigs Holding of the courses "Automation for Thermal Engineering", "Advanced and Alternative Energy Systems" and collaboration for "Thermodynamics for Mechanical Engineering - Management " Co-supervision of 3 Bachelor and 4 Master theses
05/2013-11/2015	 Project assistant, TU Wien, Vienna. At the Institute for Energy System and Thermodynamics Research on latent heat thermal energy storage systems and bimetallic finned heat exchanger tubes Design, set-up and management of a thermal energy storage test rig.
	Vocational
01/2009–07/2012	Private lessons teacher , <i>Schülerhilfe and Top Learning</i> , Wien. Teaching mathematics, physics and mechanics for students between the 5 th and the 13 th grade.
08/2006-08/2007	IT Teacher , <i>Don Bosco Vocational Training Centre</i> , Sunyani, Ghana. In the course of my mandatory Civilian Service ¹ I started up a new IT department in the vocational training centre.
	Education
01/2014-12/2019	Doctoral Programme Mechanical Engineering , <i>TU Wien</i> . PhD thesis: "Development of a Prototype Latent Heat Thermal Energy Storage System"
04/2011-08/2013	Master's Programme Mechanical Engineering, <i>TU Wien</i> . Passed with distinction Master thesis: "Latentwärmespeicher-Einrohr-System (LESY) : Auslegung, Konstruktion, Montage sowie Messungen" In-depth courses in Thermal Engineerung, Hydraulic Machinery , Rail Vehicle Design
01/2014-01/2015	Sociocracy Training , <i>Soziokratie Zentrum Österreich</i> , Wien. Module 1 and 2 completed and 5 years of experience in the sociocratic organisation Mauerseglerei (see voluntary activities)

¹In Austria young men can choose to work in the social sector abroad as an alternative to doing their compulsory military service.

08/2012-02/2013	Semester Abroad, Universidad Tecnológica Nacional, Buenos Aires.
08/2011-03/2012	TUtheTOP , <i>TU Wien</i> . High Potential Programme in collaboration with EATON and VERBUND
03/2010-12/2012	Lead the Change , <i>pioneers of change</i> , Wien. One year training for project development, change management and personal development
10/2007-04/2011	Bachelor's Programme Mechanical Engineering , <i>TU Wien</i> . Bachelor thesis: "Überlegungen zur Dimensionierung eines Flettner Rotors als Schiffssantrieb"
09/2001-06/2006	Technical Education Institute² – Automation Engineering , <i>HTL Jenbach</i> .

- Heimo Walter (heimo.walter@tuwien.ac.at) Thesis supervisor
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Publications

https://orcid.org/0000-0001-6604-5779.

- Hofmann, R., V. Halmschlager, M. Koller, G. Scharinger-Urschitz, F. Birkelbach, and H. Walter (2019). "Comparison of a physical and a data-driven model of a Packed Bed Regenerator for industrial applications". In: *Journal of Energy Storage* 23, pp. 558–578. DOI: 10.1016/j.est.2019.04.015.
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- Scharinger-Urschitz, G., M. Hameter, V. Illyés, and H. Walter (2018). "Experimental Investigation on a High Temperature Latent TES with Novel Fin Geometry". In: Proceeding of the 13th Conference on Sustainable Development of Energy, Water and Environment System - SDEWES 2018. Ed. by Faculty of Mechanical Engineering and Naval Architecture.
- Scharinger-Urschitz, G., M. Hameter, S. Krimmel, and H. Walter (14.12.2018). Latent Thermal Energy Storage - Numerical and Experimental Aspects. Luzern, Switzerland.
- Scharinger-Urschitz, G., H. Walter, and T. Bauernfeind (2019). "Novel Fin Geometry for a Latent High Temperature Thermal Energy Storage - Experimental Investigation". In: Proceedings of the 4th Thermal and Fluids Engineering Conference (TFEC 2019). Ed. by American Society of Thermal and Fluids Engineers, TFEC-2019–27516.
- Scharinger-Urschitz, G., H. Walter, and M. Haider (2019b). "Heat Transfer in Latent High-Temperature Thermal Energy Storage Systems—Experimental Investigation". In: *Energies* 12.7, p. 1264. DOI: 10.3390/en12071264.
- Urschitz, G., H. Walter, and J. Brier (2016). "Experimental Investigation on Bimetallic Tube Compositions for the Use in Latent Heat Thermal Energy Storage Units". In: *Energy Conversion and Management* 125, pp. 368–378. DOI: 10.1016/j.enconman.2016.05.054.
- **Urschitz**, **G.**, J. Brier, H. Walter, R. Mertz, F. Bleicher, and M. Haider (2015). "New Design of a Bimetallic Finned Tube for the Use in Latent Heat Thermal Energy Storage Units". In: *Proceedings of the ASME 2015 9th International Conference on Energy Sustainability*. Ed. by ASME.
- **Urschitz**, **G.**, H. Walter, and J. Brier (2015). "Experimental Investigation on Compositions and Materials for Finned Bimetal Tubes for the use in Latent Heat Thermal Energy Storage Units". In: *Proceedings*

²A HTL (Höhere Technische Lehranstalt) is a secondary education institute, where students acquire the university entry qualification and professional training at the same time.

of the 10th Conference on Sustainable Development of Energy, Water and Environment Systems -SDEWES 2015. Ed. by Faculty of Mechanical Engineering and Naval Architecture.

- **Urschitz**, **G.**, H. Walter, and M. Hameter (2014a). "Experimental Investigation of a Finned Mono Tube - Latent Heat Thermal Energy Storage (LHTES)". In: *Proceedings of the ASME 2014 8th International Conference on Energy Sustainability*. Ed. by ASME.
- (2014b). "Laboratory Test Rig of a LHTES (Latent Heat Thermal Energy Storage): Construction and First Experimental Results". In: *Journal of Energy and Power Engineering* 8, pp. 1838–1847.