Chapter 1: Fundamentals of high temperature thermal energy storage, transfer and conversion

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Abstract (100-150 words): Renewable energy generation is inherently variable. For example solar energy shows seasonally (summer-winter), daily (day-night) and hourly (clouds) variations. Thermal energy storage (TES) systems correct this mismatch between the supply and the demand of thermal energy. Hence, TES is a key cross-sectional technology for utilization of volatile renewable sources (e.g. wind and photovoltaics) and energy efficiency improvements with growing present and future importance. This chapter gives a broad overview of different options and challenges for TES utilization in the high-temperature field. The chapter structure follows the value chain of TES development from material, via component to system integration research and development aspects. The structure of this chapter is based on the classification commonly adopted in the academic literature, which distinguishes between three major TES types: sensible, latent and thermochemical storage. The chapter focuses on high temperature applications in the area of concentrating solar power (CSP) generation and operation temperatures beyond 300 °C.

Keywords (5-10): heat storage, phase change material, sensible, latent, thermo-chemical, concentrated solar power, molten salt

1. I	ntrod	uction	3			
1.1.	. M	aterial requirements and thermophysical properties	5			
1.2	. St	orage components: characteristics and key performance indicators	6			
1.3	1.3. Storage integration and applications					
2. S	2. Storage of sensible heat					
2.1.	. St	orage materials	. 11			
2	2.1.1.	Liquids as storage materials	. 11			
2	2.1.2.	Solids as storage materials	. 12			
2.2.	. St	orage component and heat transfer concepts	. 13			
2	2.2.1.	Storage concepts for liquids	. 13			
2	2.2.1.	Storage concepts for solids	. 14			
2.3.	. St	orage integration and (pre)commercial applications	. 15			
2	2.3.1.	Application and integration for liquids	. 15			
2	2.3.2.	Application and integration for solids	. 17			
3. S	Storag	e of latent heat	. 18			
3.1.	. St	orage materials	. 18			
3.2.	. St	orage component and heat transfer concepts	. 20			
3	3.2.1.	Passive PCM heat transfer concepts	. 20			
3	3.2.2.	Active PCM heat transfer concepts	. 22			
3.3.	. St	orage integration and applications	. 22			
4. Т	Therm	o-chemical Storage	. 23			
4.1.	. St	orage materials	. 25			
4.2.	. St	orage component and heat transfer concepts	. 26			
4.3. Storage integration and applications			. 26			
5. S	5. Summary and conclusion					
6. Literature						

Nomenclature

a	Thermal diffusivity	$[m^2 \cdot s^{-1}]$
b	Thermal effusivity	$[J \cdot m^{-2} \cdot K^{-1} \cdot s^{-1/2}]$
c_p	Specific heat capacity	$[J \cdot kg^{-1} \cdot K^{-1}]$
$\varDelta h_m$	Heat (or enthalpy) of melting	[J⋅kg ⁻¹]
$\varDelta h_{m,mol}$	Molar heat of melting	[J⋅mol ⁻¹]
Δh_r	Heat (or enthalpy) of reaction	[J·kg ⁻¹]
ΔH_m	Heat of melting	[J]
ΔH_r	Heat of reaction	[J]
т	Mass	[kg]
М	Molar mass	[kg·mol⁻¹]
р	Pressure	[Pa]
R	Molar gas constant	$R = 8.314472 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Т	Temperature	[K]
T_r	Reaction equilibrium temperature	[K]
T_m	Melting Temperature	[K]
T_{min}	Minimum Temperature	[K]
T_{max}	Maximum Temperature	[K]
V	Volume	[m ³]
ΔT	Temperature difference	[K]
ΔV	Volume change on melting	[m ³]
λ	Thermal conductivity	$[W \cdot m^{-1} \cdot K^{-1}]$
ρ	Density	$[\text{kg} \cdot \text{m}^{-3}]$
μ	Dynamic viscosity	[Pa·s]
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1. Introduction

There are various ways to classify thermal energy storage (TES) materials and systems. Sensible and latent heat storage utilize physical principles, whereas thermochemical storage types utilize in addition chemical reactions. Storage materials occur in different physical phases, namely as solids, liquids, gases or via a phase change. Most commonly three types of TES types are distinguished:

- Sensible heat storage results in an increase or decrease of the storage material temperature, stored energy is approximately proportional to the temperature difference in the materials. Typically, either solids or liquids are utilized. Sometimes solid-liquid mixtures are selected.
- Latent heat storage is connected with a phase transformation of the storage materials (phase change materials PCMs), typically changing their physical phase from solid to liquid and vice versa. The phase change is always coupled with the absorption or release of heat and occurs at a constant temperature. Stored energy is equivalent to the heat (enthalpy) for melting and freezing.
- **Thermochemical storage** is based on reversible thermochemical reactions. The energy is stored in the form of chemical compounds created by an endothermic reaction and it is recovered again by recombining the compounds in an exothermic reaction. The heat stored and released is equivalent to the heat (enthalpy) of reaction.

Besides the ordinary purpose of TES to match the supply and the demand of thermal energy, there are some additional key benefits on the supply as well as on the demand side for the overall systems:

- Although the heat source may be variable (e.g. solar, waste heat), TES allows for a steady supply to the heat sink with long operation time
- TES systems are often flexible in terms of the heat source (e.g., thermal, solar, waste heat, electricity) which allows for flexible hybrid operation for charging
- Rapid flux variations can be compensated (avoid strong gradients for connected components, e.g. piping, heat exchanger, boiler, turbines etc.,) which increases life time of components
- Surplus energy can be stored and does not needed to be dumped and/or the size of subsequent components can be reduced (e.g. heat exchangers, turbo machines, converters)
- For combined heat and power generation, TES can decouple heat and power generation
- TES allows improved thermal management of the system (e.g. increased start-up time, accurate preheating of components, coverage of peak demand, backup power)
- Some applications may benefit from a single advantage of TES, whereas others may utilizes several benefits simultaneously. Multiple TES use cases are often more cost effective.

Heat and cold storage has a wide **temperature** range from below 0°C (e.g. ice slurries, latent heat ice storage) to above 1000 °C (e.g. regenerator in the high-temperature industry). In the intermediate temperature range (0 to 120 °C) water is the dominating liquid storage medium (e.g. space heating). This low-temperature heat is stored for heating, ventilation and air conditioning (HVAC), as well as domestic hot water supply. The focus of the presented chapter is the temperature range **above 300** °C with applications in the industrial process heat and power generation sectors. Power generation refers to the following fields:

- Conventional power plants, e.g. flexible and hybrid operation with TES
- Electrical storage systems or plants including TES, e.g. adiabatic compressed air; pumped thermal energy storage (PTES)
- Concentrated solar power (CSP) plants.

Figure 1 defines the three major TES concepts with their physical phase or chemical reaction type, as well as typically best-suited materials for temperatures above 300 °C.



Figure X.1. Classification of the three TES concepts by physical phase and thermo-chemical reaction type for temperatures above 300 °C. Boxes with grey fields are not relevant for high temperature TES.

After the introduction, the structure of this chapter follows these three principles (sensible, latent and thermochemical) as headings. TES is a multi-scale topic ranging from cost effective **material** utilization (1), via design of a storage **component** with suitable heat transfer (2) to the integration of TES in an overall **system** (3). Each subchapter on the three technologies sensible heat, latent heat and thermochemical utilize these three subsections (material, component, system).

1.1. <u>Material requirements and thermophysical properties</u>

The following requirements should be typically met by heat storage materials:

- Large gravimetric storage capacity to minimize costs of the system (high heat capacity c_p , high latent heat Δh_m or high heat of reaction Δh_r)
- Large volumetric storage capacity as a product of the density ρ and the gravimetric storage capacity listed above $(\rho \cdot c_p, \rho \cdot \Delta h_m, \rho \cdot \Delta h_r)$ to minimize the storage volume
- Large operation temperature range for sensible heat storage (e.g. low solidification for liquids, high thermal stability, low vapour pressure)
- Simple in handling, e.g. nontoxic, non-flammable, no explosive phases, low hygroscopy
- Non-corrosive and non-erosive with respect to the containment, the heat exchanger and heat transfer enhancement structures (e.g. fins); utilization of inexpensive structural materials
- Ability to undergo ideal charging and discharging cycles with minimum hysteresis, fast response (e.g. suitable reaction kinetics for thermochemical materials) and without losses in performance in terms of storage capacity over many cycles (high cycling stability, high thermal stability, long service life, no sintering, as well as the following PCM requirements: no segregation, no subcooling and little or no supersaturation during melting)
- Suitable phase transition/chemical reaction temperature and enthalpy for PCM and thermochemical storage
- Low material price and the costs that arise upon its utilization; high availability in the required defined quality
- High thermal conductivity, diffusivity and effusivity to allow high heat transfer rates
- Small density change versus temperature, especially for solidification/melting phase change or chemical reaction to minimize thermo-mechanical stresses phenomena

Equation 1 defines the thermal diffusivity a, where λ is the thermal conductivity and ρ the density. Equation 2 defines the thermal effusivity b.

$$a = \frac{\lambda}{\rho \cdot c_p} \tag{1}$$

$$b = \sqrt{\lambda \cdot \rho \cdot c_p} \tag{2}$$

A high thermal diffusivity of the heat storage material provides a quick response to temperature differences, i.e., quick charging and discharging. A high thermal effusivity yields a large amount of heat being stored. Metals and graphite are best suited for quick charging and discharging (high thermal diffusivity a) and for a large amount of heat stored in a given time (high thermal effusivity b). Other solid materials such as stones are much less advantageous. Their respective values are smaller by an order of magnitude. Thermochemical storage system may use powder fills with even lower diffusivity and effusivity values.

It needs to be considered, that thermophysical properties are not always available and their values may differ among different literature sources. Some thermophysical property values, such as graphite values, are strongly temperature dependent. Also, impurities in the substances can change the properties considerably. For example, impurities in metals cause a drop in the thermal conductivity values.

1.2. <u>Storage components: characteristics and key performance indicators</u>

A characteristic of TES systems is that they are diversified with respect to temperature, power level and heat transfer fluids (HTFs) and that each application is characterized by its specific operation parameters. This requires the understanding of a broad portfolio of storage media, heat transfer designs and system integration aspects.

TES systems differ not only widely in terms of the temperature level, but also in terms of the heat carrier, or also known as **heat transfer fluid**. HTFs may be of single phase type (e.g. water, air, thermal oil) or two phase type with a condensation and evaporation process in the system (e.g. water/steam). The storage material and heat carrier may be one single medium. In this simpler **direct storage concept** an additional volume of hot working fluid to store heat is used. The approach demands limited research and development efforts due to its simpler design. This concept is cost-effective, as long as the medium has a low partial pressure to avoid expensive pressure vessels and the medium itself is inexpensive (e.g. molten salt). An additional solid filler material may replace expensive HTF by cheaper filler materials.

Many working fluids cannot be directly stored, the energy must be transferred to a separate storage medium and two different media as heat carrier and storage medium are utilized. This concept is usually known as **indirect storage concept**. A separate HTF and storage medium may be used for the following reasons:

- The HTF is expensive and the amount should be minimized (e.g. synthetic thermal oil, molten metal)
- The HTF has a low volumetric energy density (e.g. gas, steam)
- The HTF is pressurized (e.g. steam, water, thermal oil), whereas the larger storage volume is at atmospheric pressure for economic reasons

For the indirect storage concept, the HTF and storage media may be either of **direct contact** or **indirect contact** type. An example of the direct contact type is ceramic type regenerator with air as HTF. In some cases the direct contact of heat carrier and storage material is not economic or feasible. For example the HTF may be chemically incompatible with the storage medium or the HTF and storage medium may be at different pressure levels. In these cases, a design with indirect contact of carrier and storage medium can be utilized. The indirect contact is realized by several types of heat exchangers (e.g. embedded in the storage medium, counter flow, moving particles). Indirect storage systems require sufficient heat transfer rates from the HTF to the storage medium. In indirect storage concepts the maximum temperature of the working fluid is lower during the discharge process than during the charging process due to the unavoidable necessary temperature difference between working fluid and storage material. Hence, the minimization of temperature gradients and cost-effective designs of the heat exchanger are central issues for indirect storage concepts.

The **number of tanks**, or storage blocks, is another classification criterion. The **single tank** concept is characterized by different zones with charged and discharged storage material. An example is a sensible heat storage system with hot and cold zones (e.g. solid media regenerator with gas as HTF). Another example is a latent heat storage system based on a single tank filled with phase change material (PCM). During the charging and discharging process, the PCM of such storage is partial liquid and solid in characteristic zones. The temperature distribution within a single tank is non-uniform during charging and discharging. Hence, transient heat conduction between zones with a different temperature level needs to be addressed. For sensible heat storage with a single tank, thermal stratification is desired. The value of high temperature heat is maintained in one zone of the vessel with limited heat flow to the cold zone. In other words, due to transient internal heat conduction, the stratification is destroyed in the course of time, even in very well insulated vessels. Parasitic transient heat conduction may require an oversized storage volume to account for internal losses.

Alternatively, storage systems can utilize **two tanks**. For example, a sensible heat storage system with a liquid medium consists of two individual tanks at two distinct temperature levels and variable fluid levels. For a thermochemical storage system one tank can contain the reactant and the other tank stores the product. Compared to the single volume regenerative type storage, the two tank concept is advantageous, because the power requirements are met externally and not within the storage volume. An additional heat exchanger (sensible heat) or thermal reactor (thermochemical) can be designed according to the thermal power requirements. Hence, the two tank concept allows for a decoupling of the thermal capacity (storage in two tanks) and the thermal power (additional external component). Additional advantages of the two tank design include: flexible and independent charge/discharge operation, simplified part load operation and most importantly constant power input/output.

It is important to distinguish between the **thermal power** (e.g. kW) and the **thermal capacity** (e.g. kWh) of a storage system. The thermal capacity divided by the thermal power gives the characteristic discharge/charge time of the storage system (e.g. hours). The time scales range from less than seconds (e.g. buffering of fast radiative heat transfer via a thermal mass) to one year (seasonal storage). The storage duration is commonly in the range of minutes to hours for the temperature above 300 °C. It needs to be considered that the different storage concepts result in characteristic discharge powers, temperature and pressure levels. For example, the thermal power of the regenerator type storage is time depended. In other words, regenerator type storage systems provide discontinuously thermal power. On the other hand, other storage concepts may allow for a continuous discharge process with constant power, temperature and pressure levels (e.g. two tank molten salt concepts).

In most cases TES systems correct the **temporal** mismatch between the supply and demand of energy. In some cases TES systems aim to correct the **local** mismatch between the supply and demand of energy (transport of heat). For low temperatures, there is some interest to utilize thermochemical TES in the transport sector, but there is limited work at high temperatures. The transportation of thermal energy using vehicles with latent heat and thermochemical storage is examined (e.g. transport of industrial waste heat to consumers or thermal management in vehicles). A rare commercial example in the high-temperature field is the transportation of liquid aluminium in trucks on the road from one to another process.

Another way to classify TES is the type of **energy conversion process**. The major types are the following.

- Heat-to-heat For TES usually only reversible heat-to-heat processes are considered
- Chemical energy-to-heat A special kind of heat storage media are fossil or nuclear fuels, such as wood, coal, oil, or uranium. These are characterized by a very high energy density compared to TES and an **irreversible** application. Since storage is understood in this article as a **reversible** process which can be repeated more or less indefinitely, the irreversible storage processes will not be treated here.
- **Electricity-to-heat** This process is utilized by night storage heaters or power-toheat-to-power systems and this charging option is also treated as TES system.

For high temperature TES various basic concepts have been suggested. These concepts can be described by various technical criteria. These criteria or key performance indicators include the following.

- Thermal power provided during the discharging process, power transferred during the charging process
- Capacity of the storage unit, i.e. total energy provided during the discharge process
- Temperature of heat provided during the discharge, maximum temperature accepted during charging process
- Frequency of charging/discharging cycles

- Reaction time needed to provide nominal load
- Thermal losses, parasitic power needed during charging/discharging process
- Exergetic efficiency

The multitude of criteria makes a direct comparison of TES systems difficult. Values like thermal power or temperature might also be time-dependent for certain storage concepts. Storage units must be adapted both to the heat source and the heat sink. The requirements may also differ between the source and sink (e.g. in terms of thermal power, reaction, heat exchanger temperature difference, frequency, reaction time). Dominating factors to select a suitable TES technology is typically the temperature and pressure level of the HTF.

1.3. Storage integration and applications

High temperature TES development is currently driven by the need to improve the energy efficiency and the implementation of volatile renewable sources into the electric grid retraining quality of bulk power supply. The capability of storing high-temperature thermal energy can lead to economically competitive design options compared to other electrical storage solutions (e.g. battery storage). **Concentrating solar power** (CSP), also known as Solar Thermal Electricity (STE) is a commercial technology that produces heat by concentrating solar irradiation. Commercial systems utilize sensible heat molten salt storage systems. This heat is typically used to generate electricity via a subcritical steam turbine (Rankine cycle). Figure 2 shows typical cycle conversion efficiencies taking typical CSP maximum temperatures of either about 390 °C or about 550 °C. It can be also seen that the cycle efficiency could increase, if the maximum operation temperature would be raised.



Figure X.2. Conversion efficiencies of thermodynamic cycles depending on the hot temperature (40 °C is assumed for the cold temperature), redrawn from (Siegel 2014) within this work.

Hence, alternative thermodynamic power cycles are examined. For electricity generation from high-temperature TES the following cycles are of interest (Stein 2017, Forsberg 2007, Ahn 2015):

- Rankine cycle with steam
 - Conventional (subcritical)
 - Supercritical Rankine cycle
- Stirling cycle
- Closed-loop Brayton cycle
 - Supercritical CO₂
 - o Helium, nitrogen

- Combined cycle with topping and bottoming cycles, e.g. combined cycle gas turbine (CCGT)

Other innovative converter technologies which could potentially convert heat from TES to electricity include thermoelectric, thermophotovoltaic, thermionic, alkali metal thermal to electric (AMTEC) and liquid metal magnetohydrodynamic (LMMHD) conversion (Fritsch 2015, Bauer 2011a).

The commercial status of high-temperature TES makes CSP a unique application. By storing the thermal energy and/or using hybridization CSP is able to firmly deliver electricity (an optionally heat) on demand (Figure 3). The ability to provide electricity on demand makes CSP stand out from other renewable energy technologies like photovoltaics or wind. Further advantages of TES integration include:

- Although additional TES is installed the overall levelized cost of electricity (LCOE) can be reduced (mainly due to longer operation hours of the power block)
- Rapid flux variations can be compensated (avoid strong gradients for connected components, e.g., piping, heat exchanger, boiler, turbines etc.,) which increases the lifetime of components
- The size of subsequent components, e.g., evaporator, condenser, boiler, turbines, can be reduced
- TES allows improved thermal management of the solar system (e.g., increased start-up time, accurate preheating of solar steam cycle, avoid surplus energy, cover peak demand);



Figure X.3. Basic layout of a concentrated solar power (CSP) plant with integrated thermal energy storage. Grey text shows additional options to extend the concept.

TES can be integrated in **conventional power plants** in order to increase the flexibility. This allows for the accommodation of a larger share of volatile renewable power from wind and photovoltaics. Benefits of conventional power plant concepts with an integrated high-temperature TES include:

- Higher flexibility of electricity generation and thermal management of the power plants due to TES implementation (e.g. faster gradients, reduction of minimum load and improved part load, component preheating, improved availability, backup heat)
- Hybrid operation, or "fuel switch", e.g. combination of fuel combustion and power-toheat (P2H) from volatile wind or photovoltaic electricity combined with TES
- Conventional combined heat and power (CHP) unit operate either on heat or electricity demand. Often there is a fixed ratio of heat and electricity generation which can make such operation for varying heat and electricity demand inefficient. TES can decouple the generation of heat and power for CHP

TES can also provide these listed services above to the application fields of electrical storage for the grid and process heat sector and these applications are discussed in the following text without going into details of potential multiple use cases in terms of flexibility, hybrid operation and CHP, as well as heat upgrade for thermochemical storage.

Bulk grid-connected **electrical storage** is dominated by pumped hydroelectric energy storage (without TES). The potential growth of pumped hydro energy storage is limited by geographic dependencies and the environmental impact. Hence, massive electrical storage including a TES is a major option to further enlarge the implementation of volatile renewable

sources (mainly wind and photovoltaics). Currently several electrical storage concepts including large-scale TES are examined [Steinmann 2017]. These non-commercial concepts include the following:

- Electrothermal energy storage (ETES), also called power-to-heat-to-power (P2H2P) concept, utilize a P2H component for charging, a TES and different devices for discharging. For power cycles, such as Rankine and Brayton, the efficiency is limited by the Carnot efficiency. Although the discharge step of turbomachines limits the efficiency, the P2H component for charging can be relatively inexpensive and hence P2H provide an efficient way to absorb short and large peak power (e.g. photovoltaics during midday). Further advantages include a high life expectancies in the range of 20–30 years, low capacity-specific costs (€·kWh⁻¹), a low environmental impact and flexibility regarding sites. At the time of writing, the conversion of conventional coal power plants in Germany into ETES is considered. One major motivation is the re-use of existing infrastructure (steam turbine, generator, cooling tower, grid-connection).
- **Pumped thermal energy storage (PTES)** utilize an electrically driven heat pump during charging to create two distinct heat storage reservoirs. During discharging, this temperature difference is used to operate a thermal cycle. There are several thermal cycles (e.g. Brayton, Rankine), working fluids (e.g. air, CO₂, water-steam) and temperature levels, as well as different storage media (e.g., liquid air, ice, water, molten salt, rocks, ceramics). In the low temperature region liquid air energy storage (LAES) is a major concept. The advantages of PTES are similar to the ETES concept: high life expectancies, low capacity-specific costs, low environmental impact and site flexibility. Utilization of the heat pump makes PTES an isentropic concept with a higher potential efficiency (theoretically 100%) at the expense of a more complex system compared to ETES.
- **Compressed air energy storage (CAES)** utilize electricity for air compression, a closed air storage (either in natural underground caverns at medium pressure or newly erected high-pressure vessels) and an air expansion unit for electricity generation. A few CAES installations exist and typically turbomachines are utilized. In an advanced concept, an additional TES can store compression heat during charging and preheats air during discharging in order to increase the round trip efficiency. This isentropic concept has also a theoretical efficiency of 100% and is called **adiabatic compressed air energy storage (A-CAES)**.

Another application field is the improvement of the energy efficiency in the **process heat industry** by TES integration. Particularly the high-temperature energy intensive industries like iron and steel, non-ferrous metals, cement, ceramics, glass and chemical sectors are of interest. TES may be integrated in the on-site CHP plants or directly within the process. Processes and use cases for TES are diverse. Examples are regenerative type TES in flue gas and air supply streams, improved heat integration of batch processes, backup heat, buffering of fluctuating waste heat streams and stabilizing steam supply, as well as improved electrical load management with P2H and TES.

For further reading, several books on the subject of TES are available providing overviews and theoretical background (Turner 1978, Schmidt 1981, Beckmann 1984, Garg 1985, Dinter 1991, Dincer 2002, Fisch 2005). The following literature focuses specifically on high temperature TES (Elliott 1977, Geyer 1991, Herrmann 2002, Gil 2010, Medrano 2010, Tamme 2009, Mohan 2019).

2. Storage of sensible heat

Sensible heat always results in an increase or decrease of the material temperature. All materials have a capability of absorbing and storing heat due to the fact that they have a mass m and a specific heat capacity at constant pressure c_p . The heat capacity increases with temperature. The underlying theory is described by the Debye model. For a temperature difference $\Delta T = T_2 - T_1$ this heat (or enthalpy) amounts to ΔH_m (Equation 3).

$$\Delta H_m = m \cdot c_p \cdot (T_2 - T_1) = m \cdot c_p \cdot \Delta T \tag{3}$$

 T_2 denotes the material temperature at the end of the heat absorbing (charging) process and T_1 the temperature at the end of the heat release (discharging). It is important to note that the specific storage costs can be reduced considerably, when the storage is implemented in systems with a larger temperature difference ΔT , as the capacity of a molten salt storage is directly proportional to the temperature difference between the hot and the cold temperature. For high enough temperatures and pure solids (especially heavy elements), the specific heat per mole of a substance is about 3R (Dulong – Petit rule), with *R* being the molar gas constant ($R = 8.31441 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). The volumetric heat capacity $\rho \cdot c_p$ of non-porous solids and liquids is typically in the range 1.5 to 6 MJ·m⁻³·K⁻¹ (Bauer 2012, Cverna 2002).

2.1. Storage materials

2.1.1. Liquids as storage materials

Liquids offer the advantage of a possible use as both TES medium and HTF. In addition to the listed properties in Section 1.1, further key properties of liquids related to thermophyiscal and physicochemical properties are:

- Minimum operation temperature T_{min} in °C which is typically defined by the liquidus temperature, melting temperature T_m or a high viscosity
- Maximum operation temperature T_{max} in °C which is typically limited by thermal decomposition, vapour pressure or metallic corrosion
- Dynamic viscosity μ in Pa·s. A low viscosity is desired for pumping

At low temperature, the most widely applied medium is **water**. Applications include storage tanks for hot water in industry and dwellings, seasonal store for solar energy and aquifer store operating at maximum temperatures of 150 °C at low or ambient pressure. At higher temperature the utilization of pressurized water is limited by the critical point of saturated water (374°C, 221 bar). State of the art for TES used in process heat applications is the steam accumulator technology. The costs are dominated by the pressure vessel. Due to the limited maximum temperature, water systems are not considered further in this chapter.

Thermal oil is a common heat transfer fluid and has also been used as a liquid storage material. For example, mineral oil can be used at ambient pressures up to about 300 °C. Synthetic oils are thermally stable up to 400 °C, but synthetic oils have higher prices and at higher temperatures they require pressure vessels. Hence, above 300 °C thermal oil is typically uneconomic.

For temperatures above 150 °C, **molten salts** are attractive candidates for sensible heat storage in liquids. The major advantages of molten salts are low costs, high thermal stability and low vapour pressure. The low vapour pressure results in storage designs without pressurized vessels. In general there is experience with molten salts from a number of industrial applications related to heat treatment, electrochemical reactions and heat transfer. The application of salts requires the consideration of the lower temperature limit defined by the melting temperature. One major difficulty with molten salts is unwanted freezing during

operation. Freezing must be prevented in the piping, the heat exchanger and in the storage tanks. Hence, often auxiliary heating systems are required. The thermal stability of the salts and metallic corrosion limit the upper temperature. Salt mixtures, rather than single salts, have the advantage of a lower melting temperature. These mixtures can have similar thermal stability limits as the single salts of the mixtures. Hence, salt mixtures, such as eutectics, can have a wider temperature range compared to single salts. For solar thermal power plants, alkali nitrate salt mixtures, and to some extend alkali nitrite salts, are the preferred candidate fluids for TES. Typically a non-eutectic salt mixture of 60 wt% sodium nitrate and 40 wt% potassium nitrate is utilized. This mixture is commonly called **Solar Salt**. The eutectic mixture has a liquidus temperature of about 250 °C and the thermal stability limit is at about 560 °C. Many salt mixtures exist (Janz 1978) and major other candidates for higher operation temperatures are K₂CO₃-Li₂CO₃-Na₂CO₃ (35-32-33 wt%) in a range from 400 – 650 °C; KCl-MgCl₂ (61-39wt%) from 430 °C to more than 700 °C; KF-LiF-NaF (59-29-12 wt%) from 460 °C to more than 700 °C (Bauer 2013).

For high-temperature storage systems, **molten metals**, such as sodium ($T_m = 98$ °C) and lead ($T_m = 327$ °C) are potential candidates (Niedermeier 2018, Fritsch 2015). Experience with these metals exists from the nuclear reactor field. Major advantages are the high thermal stability and the high thermal conductivity (or good heat transfer properties) of these metals. Sodium has the most favourable thermophysical properties. However, at elevated temperatures the reactivity of alkali metals with air and water is high and requires careful design and handling.

Further potential liquid sensible heat storage materials include **molten glass** in the range 400-1200 °C (Elkin 2014) and **molten sulphur** in the range 200-600 °C (Barde 2018).

At elevated temperatures (>300 °C), combined storage in liquids and solids is also of interest. Table 1 lists some commonly considered material systems.

5 5 5 5								
Filler material as solid storage medium	Heat transfer fluid and liquid storage medium	Literature						
Cast iron, Natural stone (granite, silica, quartzite)	Thermal oil	Bauer 2012, Esence 2017						
Graphite	Halogen salts	Forsberg 2007						
Natural stone (basalt, quartzite)	Nitrate/nitrite salts	Esence 2017, Martin 2018, Pacheco 2002b						
Natural stone (quartzite), graphite, alumina	Sodium, Lead, Lead-Bismuth	Niedermeier 2018, Fritsch 2015						

Table X.1: Material systems for combined heat transfer fluid with filler.

2.1.2. Solids as storage materials

Solid materials can be utilized in a wide temperature range and heated up to very high temperature (e.g. ceramics in Cowper regenerators to more than 1000 °C). Solids are often chemically inert and have a low vapour pressure. In addition, the containment can often be simpler compared to systems based on liquids (Tamme 2009). Solid storage materials can be classified as metals and non-metals, as well as natural and manufactured materials.

Natural materials in the form of rocks and pebbles are abundant and cheap. For high temperatures, the thermo-mechanical stability of the solids is important. Here, rocks such as granite, basalt and quartzite, as well as pebbles can have suitable properties.

Of the manufactured solid materials, various **ceramics** are widely used as heat storage materials. At higher temperatures, refractory bricks based on oxides (silica, alumina, magnesia and iron oxide - feolite), carbonates (e.g. magnesite) and their mixtures are commercially utilized in applications such as Cowper regenerators, night-storage heaters and

tiled stoves. As a low cost alternative, also slag is considered as storage material (Krüger 2019).

For high temperatures up to 500 °C, **concrete** is another potential sensible heat storage material, because of its low cost due to inexpensive aggregates, the availability throughout the world and the available and simple processing route via casting (Laing 2011).

Graphite is another potential solid media for sensible heat storage. Graphite has a high thermal diffusivity and it can be heated up to very high temperatures, but above about 400 °C it requires an inert atmosphere to prevent oxidation.

Metals typically exhibit higher thermal conductivities but are less attractive from an economic point of view compared to non-metals. This high conductivity is advantageous in terms of a fast charge and discharge process of the storage system. High conductivity metals, such as aluminum and copper, can be used in electronics as a heat sink and for thermal management. Cast iron is an alternative material with a high thermal conductivity, high volumetric heat capacity (energy density) and low capital cost.

Abundant **solid salts**, such as sodium chloride ($T_m = 801 \text{ °C}$) and sodium sulphate ($T_m = 884 \text{ °C}$) could also be potentially utilized. Critical aspects are typically creep, mechanical strength, manufacturing processes and compatibility with the HTF.

2.2. Storage component and heat transfer concepts

2.2.1. Storage concepts for liquids

The storage approach using liquids can be realized with a single tank, two tanks or several tanks. The two tank concept (2T) consists of two individual tanks at different temperature and fluid level (Figure 4). A significant advantage of the 2T concept is the very constant inlet and outlet temperatures during the entire charging and discharging process. Also, the thermal power (pumps and heat exchanger size) and the thermal capacity (storage tank size) can be freely designed. For the single tank concept, density difference between hot and cold fluid allow for thermal stratification with a thermocline zone between the hot fluid and the top and the cold fluid at the bottom. This is achieved by either natural stratification (TC concept in Figure 4) or additional filler materials. Liquid storage medium can create the predominate cost of the entire storage system. In these cases low-cost solid filler materials can replace expensive liquid storage materials and also can improve stratification. In this thermocline filler (TCF) concept sensible heat storage takes place in the solid and the liquid and for heat transfer between these two phases the thermocline zone (or single tank) is mandatory. For charging the flow direction is from top to bottom (shown in Figure 4) and for discharging the flow direction is from bottom to top (not shown). The heat exchanger shown in Figure 4 is typically a shell-tube type heat exchanger, but could be also another type (e.g. plate heat exchanger, direct-contact) or replaced by an electrical heater.

CSP research focuses also on several sensible storage concepts with **combined storage in liquids and solids**. The main aim is to displace expensive liquid storage medium by cost-effective solids by TCF concept (see Table 1 for material pairs and literature).



Figure X.4. Basic concepts for liquid storage concepts: Two-tank (2T), Thermocline concept with natural stratification (TC), Thermocline concept with moving barrier to improve stratification and losses (TCMB) and thermocline filler concept to replace some liquid volume (TCF). For simplicity only the charging process is indicated. Typical pros and cons are also given.

2.2.1. Storage concepts for solids

The heat transfer concept of storage systems using solid materials is usually based on an additional HTF (e.g. water, steam, air, oil, molten salt) for the charge and discharge process. The HTF may be operated either in direct contact (e.g. Cowper regenerators in the high-temperature glass and steel industry) or indirect contact (e.g. via a heat exchanger) with the solid storage material.

In a **direct contact** storage system, there is no intervening wall between heat transfer fluid and storage medium. Direct contact design is realized as a regular array of checker bricks (Figure 5 RS concept) or packed bed of solid particles in a container, such as a pebble bed, a rock pile or with saddle rings (RB). Typical heat carriers in direct contact are air, flue gas or inert gases. These beds and checkers provide a large surface area for heat transfer.

Packed bed storage with direct contact to the HTF (concept PB in Figure 5) systems are examined by several research institutes mainly for CSP applications (Esence 2017, Dreißigacker 2010). The major motivation arises from the low investment costs of the packed bed compared to ceramic refractory checkers. Design aspects of packed bed storage include for example selection of durable inventory, storage utilization factor, operation costs for gas flow, lifetime, thermo-mechanical behaviour of the bed itself and with walls under cycling condition, as well as HTF pressure losses and flow design (Krüger 2019).

For solar tower systems, receivers using **solid moving particles**, such as spherical sintered bauxite proppants or sand, as a heat transfer fluid and storage medium are examined. Potentially, a two tank sensible TES system with cold and hot solid particles could be used (concept MP see Figure 5). Research and development design aspects include the long-term thermo-mechanical stability of the particles, parasitic loads for particle transport and effective heat transfer between particles, working fluids, optimization of the overall cycle and component development. Component development includes the solar receiver (e.g., falling

particle, centrifugal receiver), the steam generator (e.g. fluidized bed or moving bed) and qualification of particle transport solutions (e.g. screw conveyor for lifting).

In some cases the direct contact of heat carrier and storage material is not economic or feasible, for example if the heat carrier is pressurized (e.g. steam) or incompatible with the storage medium. In this case, a design with **indirect contact** of carrier and storage media can be utilized. Sensible indirect contact heat storage in solid media can be realized by the integration of a heat exchanger into the storage material. For example, **concrete storage** systems intended for parabolic through power plants using synthetic oil as heat transfer fluid have been developed. This storage unit is operated between 290°C and 390°C with daily charging and discharging cycles. For this application, a parallel steel tube heat exchanger design using a concrete with aggregates, sand and a low level of binder made of blast furnace cement and flue ash is considered to be the most cost-effective solution (Laing 2008, Bahl 2009, Laing 2010).



Figure X.5. Basic concepts for solid storage concepts: Regenerator with structured inventory, such as refractory checker bricks with direct contact to gases (RS), Regenerator with a packed bed, e.g. natural stones, saddle rings with direct contact to gases (RB) Regenerator with a tube with direct (e.g. graphite block with holes) or indirect contact with an additional tube register made of steel (RT) and moving solid particle concept for example with ceramic proppants (MP). For simplicity only the charging process is indicated. Typical pros and cons are also given.

2.3. Storage integration and (pre)commercial applications

2.3.1. Application and integration for liquids

Figure 6 plots typical integration options of sensible heat storage systems with liquid media. The heat source may be concentrating solar heat, waste heat, combustion heat and electricity. Also, hybrid operation with more than one heat source is feasible. For high-temperature TES the heat sink is typical a power cycle (e.g. Rankine) or industrial process heat. Also, combined heat and power is feasible with low grade heat or process steam supply. Either single or two tanks can be utilized (see Figure 6 top and bottom). Furthermore, either a single heat exchanger or two separate heat exchanger for charging and discharging can be employed (see Figure 6 left and right). The concept with two heat exchangers has the following advantages:

- Constant power and temperature level during charging and discharge (a single heat exchange leads to different temperature levels at the heat sink, if the TES is bypassed or discharged)
- The heat exchanger can be specifically designed for the heat source and sink (e.g. different fluids, different power levels, different temperature difference in heat exchanger)
- Heat source and heat sink are fully decoupled via the TES



Figure X.6. Basic schemes of liquid TES cycles (bold lines) with single heat exchanger (left) or separate heat exchangers for charging and discharging (right), as well as with two-tank (top) and single tank (bottom) technology.

For the CSP parabolic trough technology, the Andasol type power plants in Spain are large-scale commercial examples of the **indirect storage** with the single heat exchanger concept and two tanks. Typical systems have an output power of 50 MW_{el} and storage capacity of 8 h or about 1000 MWh_{th} (Figure 7 right) (Relloso 2009, Kolb 2010).

A large scale example of a **direct storage** concept is the CSP tower technology with different commercial projects completed and under-construction at the time of writing (e.g., Solar Two, Gemasolar, Crescent Dunes, Aurora, Atacama1, NOOR3). The system contains a solar central receiver (heat exchanger 1) and a molten salt steam generator (heat exchanger 2). The largest systems have more than 100 MW_{el} and a storage size of up to 17 h (Figure 7 left).



Figure X.7. Simplified CSP scheme of power tower CSP plant with direct molten salt storage and heat transfer system (left) and parabolic trough power CSP plant with indirect molten salt storage system (right).

2.3.2. Application and integration for solids

Large-scale regenerator type storage systems with refractory checker bricks in direct contact with gases are employed commercially in the **iron and steel**, as well as in the **glass industry** since several decades. Figure 8 shows the implementation in the glass industry as an example for air preheating and flue gas heat recovery. During the first operation period Regenerator 1 is discharged and Regenerator 2 is charged (shown in Figure 8). During the second operation period the flow direction is reversed (Regenerator 2 is discharged and Regenerator 1 is charged; not shown in the Figure 8).

Central tower CSP plants using air as a HTF are in a research and development phase (Figure 8). A pilot storage system with refractory checker bricks is integrated into the Solar Power Tower Jülich, Germany. The pilot plant uses an open volumetric solar receiver. In its primary cycle, air at atmospheric pressure is heated up to temperatures of about 700 °C. This solar heat then powers a steam generator, producing steam at 100 bars and 500 °C and driving a 1.5 MW_{el} steam turbine-generator set. In parallel to the steam generator and receiver, the heat storage is integrated into the power cycle (Figure 8) (Zunft 2009, Zunft 2010, Dreißigacker 2010).



Figure X.8. Scheme of a commercial molten glass furnace with two alternately charged/discharged regenerator type storage systems (left). Schematic plant layout of the DLR CSP Tower Jülich with integrated regenerator storage with 6 MWh for 1 h and temperatures from 120-680 °C (right).

3. Storage of latent heat

Materials for the storage of latent heat are also named phase change materials (PCM), because of the fact that they change their physical phase from solid to liquid and vice versa. The phase change is always coupled with the absorption of heat when the solid melts — heat of melting — and a heat release when the liquid solidifies. The phase change occurs at the melting temperature T_m . At that temperature, these materials melt when heat is added, but do not exhibit a rise in temperature (latent heat). The most prominent advantage of storage concepts using the latent heat is the option to store energy within a narrow temperature range close to the phase change temperature.

A change of one crystalline form into another without a physical phase change may also be considered as storage of latent heat (or heat of fusion). This heat of solid-solid phase changes (rearrangement of crystalline forms) is typical smaller compared to the heat of melting and solidification. Although enthalpies are large, the liquid-gas phase change is not utilized for latent heat storage due to the large volume of the gas phase. Hence, in most cases the heat of the solid-liquid phase change is utilized. The heat (or enthalpy at p = const.) stored with a phase change amounts to the latent heat (enthalpy) of melting Δh_m in J·kg⁻¹.

A rough estimate of the latent heat of the various phase change materials can be obtained from the following formula. For many semiconductors, eutectic, and inorganic compounds, the molar heat of melting $\Delta h_{m,mol}$ is within the range given in Equation 4, where the melting temperature T_m is given in Kelvin and R is the molar gas constant.

$$2.5RT_m < \Delta h_{m,mol} < 5RT_m \tag{4}$$

Equation 4 shows that the heat of fusion increases with the phase change temperature and that compounds with a low molar mass are favourable in terms of large heat of fusion values in the relevant unit $J \cdot kg^{-1}$. When a material is heated over a larger temperature difference the total heat is the sum of latent plus sensible heat in the solid and liquid phase. The heat of fusion is typically larger than the sensible heat, if smaller temperature intervals are considered. It is important to note that the melting temperature is material-specific and the material is selected accordingly.

Books on the subject of latent heat storage or phase change materials include the following (Humphries 1977, Lane 1983, Garg 1985, Lane 1986, Mehling 2008). Review articles have been presented by the different authors (Abhat 1983, Farid 2004, Zalba 2003, Sharma 2005, Demirbas 2006, Regin 2008, Kenisarin 1993, Agyenim 2010). Overviews of high temperature latent heat storage material and system developments have also been written (Birchenall 1980, Hoshi 2005, Tamme 2008, Kenisarin 2010, Crespo 2018).

3.1. Storage materials

PCMs are mainly characterized by a suitable phase change temperature and enthalpy for the application. Further PCM requirements are listed in Section 1.1.

As **low temperature PCM** for cooling of buildings water/ice, slurries using a solution of water-salt (brine) and water-glycol are utilized. In the temperature range up to 150 °C paraffins and salt hydrates are utilized (e.g. transport containers, thermal management of electronic equipment, pocket heater, clothes, heating/cooling of buildings). At temperatures above 120 °C, critical aspects of organic PCMs include the long-term thermal stability, the reactivity with oxygen and the high vapour pressure. At higher temperatures typically other material classes have suitable properties.

Various **anhydrous salts** and mixtures are available for melting temperatures larger than 130 °C. The cations are mainly alkali (e.g. Li, Na, K) and alkaline earth (e.g. Ca, Mg) metals.

Anions which are typically considered include nitrates, nitrites, hydroxides, bromides, carbonates, chlorides, sulphates and fluorides. Many anhydrous salts are miscible and this results in a large variety of potential single salts and salt mixtures (binary and ternary systems). Figure 9 presents a selection of characteristic materials PCMs with their enthalpy and melting temperature (above 300 °C). Many more PCMs can be found in literature (Sarvghad 2018, Birchenall 1980, Janz 1978, Bauer 2012). Some salt have low material prices, but the thermal conductivity is low with typical values around or lower than 1 W·m⁻¹·K⁻¹. Hence, for salt-based PCM storage typically concepts to increase the heat transfer are developed.

The single elements, such as **Si**, **Mg and Al** as well as their alloys are also potential PCM candidates (Figure 9). Lithium hydride with a very low molecular weight has an exceptionally high melting enthalpy. Metals and alloys typically have higher thermal conductivities compared to salts (Sarvghad 2018, Birchenall 1980).



Figure X.9. Properties of selected inorganic high-temperature PCMs: Salts and salt mixtures (full circles) and metals and other alloys (empty circles).

3.2. Storage component and heat transfer concepts

The development of a latent heat storage system starts with the selection of the PCM. The temperature of the phase change corresponds to the specific application. PCM storage requires a suitable heat transfer concept in order to minimize the temperature difference between PCM melting temperature and HTF temperature. This is especially true for PCMs with low thermal conductivity. The thermal conductivity of the PCM affects significantly the power density and the heat transfer design of the system. The charge and discharge power of the storage system corresponds to the melting and solidification time of the PCM. Figure 10 gives an overview of PCM storage concepts to enhanced heat transfer between the storage material and HTF (Zalba 2003, Sharma 2005, Tamme 2008, Steinmann 2008, Regin 2008, Agyenim 2010, Liu 2012).



Figure X.10. Heat transfer enhancement concepts for latent heat storage systems.

Analytical solutions for the non-linear problems of melting and solidification date back to the 19th century. Analytical solutions of the melting and solidification are known only for a few special cases with simple geometries (e.g. plane wall, tube) (Yao 1989, Alexiades 1999). More complex geometries and other effects like free convection require numerical methods (Baehr 2006, Bauer 2012, Bauer 2011b, Vogel 2019).

3.2.1. Passive PCM heat transfer concepts

There are two general types of extended heat transfer surface concepts. One approach is the **encapsulation** of the PCM. The terms micro-encapsulation and macro- encapsulation refer to the physical size of the capsules. Macro- and micro-capsules prevent the PCM from leaking in the liquid phase. Micro-capsules may be embedded in a solid matrix or suspended in a heat transfer fluid. The latter concept is also known as micro-encapsulated PCM slurry. The large heat transfer surface area of the micro-capsules results in high heat transfer rates. Similarly, a heat transfer fluid, such as molten salt or molten metals, could be potentially surround macro-capsules in order to achieve a high transfer rate. Design criteria of the capsule include the following:

- Wall thickness (flexible or stiff design)
- Inside and outside pressure levels
- Compatibility of capsule material with the PCM and heat carrier fluid
- Void volume for the expansion of the PCM during melting
- Thermo-mechanical stress and long-term stability of the capsules

Encapsulation is commercially employed at low temperatures (<120 °C) where polymers can be used. Higher temperature materials for capsules include for example metals, graphite and ceramics. Basically, containers for PCM can be either thin-walled (flexible) with equal pressure inside and outside or thick-walled (stiff) with different pressures. Often a minimum thickness to ensure a sufficient life expectancy regarding corrosion is required. Consequently, a design using flexible containers is not always possible. A significant drawback of stiff capsules is the necessity to include a gas volume to compensate the expansion of the PCM during melting/solidification. For nitrates it was found that only about 60 % of the volume could be filled with PCM (Steinmann 2008). Other critical design aspects may be leak tightness and a significant amount of required capsule material.

Another concept with extended heat transfer surface utilizes additional **conductive structures to enhance heat transfer**. The concept aims to reduce the distances for heat transfer in the low conductive PCM. Examples of structures include fins, foams, meshes, wires and fibres. Dispersed conductive particles show a low interconnection. Hence, they provide a less effective heat transfer path compared to interconnected structures, if the same structure volume is assumed. Design criteria of conductive structures to enhance heat transfer include the following:

- Compatibility of conductive structures and PCM
- Minimization of contact resistance between the conductive structures and heat carrier structure (e.g. tube)
- Thermo-mechanical stress due to density changes of the PCM and long-term stability of the structure
- Optimization of the geometry of the conductive structure (e.g. avoidance of large physical distances between structure and PCM, minimization of material utilization, suitable interconnection of the structure)

An important ratio is the volume fraction of the conductive structure to the total volume (PCM and conductive structure volume). The volume specific costs of conductive structure in $\varepsilon \cdot m^{-3}$ can be compared to the volume specific costs of PCM to estimate the acceptable fraction of structure materials. Typical conductive structure materials include aluminium, graphite, steel and copper.

The **finned tube** design is advantageous for applications with high temperatures, corrosive PCMs and pressurized HTFs. By using finned tubes, the effective surface of the tube is extended. The aim is the replacement of expensive pressure pipes by less expensive non-pressurized thermally conductive structures. The geometry of the fin depends on the specific power requirement. There are several optimization parameters for fin geometry, such as longitudal or axial fins, spacing and thickness of fins (Steinmann 2008, Laing 2010, Bauer 2011b).

Heat transfer enhancement can be also achieved by **conductive composites**. These composites combine the properties of a high latent heat of a PCM and a good thermal conductivity of an additive. An aspect of interest is the stability of the composites without phase separation after several melting and solidification cycles. PCM composites may be prepared by compression, infiltration or other process.

Also of interest are form-stable **composite with direct contact to the HTF**. If the composites are sufficiently small or provide channels for HTF, high heat transfer rates can be achieved. At high temperatures, form-stable salt-ceramic composites have been developed. Here, anhydrous salts are utilized as a PCM and a ceramic matrix provides form stability. Salt-ceramics with PCMs with phase change temperatures in the range 700 to 900 °C were considered. The HTF was air in direct contact to the salt-ceramic composites (Tamme 1991).

3.2.2. Active PCM heat transfer concepts

Finally, some other methods exit to actively enhance heat transfer. An **intermediate heat transfer fluid** can transfer thermal energy between the primary HTF and the PCM. An intermediate "heat pipe" system based on the evaporation and condensation of a suitable intermediate HTF would be very suitable. In this concept, both the intermediate HTF and the PCM undergo a phase change. In this way large temperature differences do not occur and the exergy efficiency of the charging and discharging process can be high. If the PCM and the intermediate HTF can operate in direct contact, the primary heat exchanger of this concept can be much smaller compared to a heat exchanger directly embedded in the PCM. There are several requirements with regard to intermediate HTF. The temperatures for boiling and condensation of intermediate HTF must be adapted to the melting temperature of the PCM. For example Adinberg discusses further details of the so called reflux heat transfer storage concept (Adinberg 2007).

The **transportation/moving of solid PCM** is another concept that can be used to address the heat transfer limitations caused by frozen PCM around the heat transfer structure. Transportation of solid PCM allows a storage system design with two tanks. One tank contains liquid PCM and the other tank stores the solid PCM. In this way the heat exchanger and the storage volume is separated. The heat exchanger of such design can be smaller compared to an embedded heat exchanger in the PCM. Cooling application employ the concept of transportation of solid PCM in the form of ice slurries (Ure 2011). At high temperature the transportation of solid PCM is also researched. There are several active feasible heat exchanger designs such as screw heat exchanger, scrappers and intermediate warming of the exchanger surfaces (Pointner 2016, Ure 2011, Crespo 2018).

3.3. <u>Storage integration and applications</u>

First prototypes in the scale of several 100 kWh have been developed for high-pressure steam storage. Hence, this application is discussed in more detail. The melting temperature for candidate PCMs corresponds to the water/steam condensation/evaporation temperature in a range from 120 °C (2 bar) to 340 °C (150 bar). The latent heat storage systems utilize a fined heat exchanger pipe for heat transfer enhancement that is integrated into the PCM. During the charging process, the steam condenses inside the pipes and the PCM melts. During discharging, the solidifying PCM releases heat, the water evaporates inside the pipes and steam is generated (Tamme 2008, Steinmann 2008). Applications of these steam storage systems include the areas of direct steam generation CSP plants (Seitz 2017) and high-pressure steam backup systems (Johnson 2017).

Other potential applications and PCM storage concepts have also been examined:

- Passive PCM steam storage for the energy intensive industrial process heat sector (Tamme 2008)
- Cascaded PCM storage units to enlarge the temperature interval for single-phase heat carriers. In this system various PCMs with different melting temperatures can be composed to form a cascaded system the CSP application (Michels 2006).
- PCM systems using a melting range rather than a single melting point for single phase heat carriers for the CSP application (Bauer 2010)
- Thermocline storage with partial PCM sections to stabilize the outlet temperatures for the CSP application (Crespo 2018)
- Electrical storage based on Power-to-heat-power technology, e.g. with steam power cycles (Jockenhöfer 2018) and thermophotovoltaic conversion (Datas 2016)
- CSP systems with high-temperature PCM: for example Dish-Stirling (Andraka 2015) and Fresnel optical fibre thermophotovoltaic conversion technology (Datas 2013).

4. Thermo-chemical Storage

Chemical energy storage systems utilize the enthalpy change of a reversible chemical reaction. The interest in these systems is motivated by the option to store energy at higher energy densities than other TES types (Wenthworth 1976, Mar 1980, Sizmann 1980, Felderhoff 2013, Linder 2015, Prieto 2016, Dizaji 2018). Other attractive features of thermochemical storage are:

- It is feasible to store reactants and the product at ambient temperature to avoid thermal losses. This feature is for example attractive for long-term storage (e.g. seasonal).
- Compared to sensible and latent heat systems, thermochemical storage can have different temperature levels for the charge and discharge process via pressure changes of the gas phase. Hence, it is feasible to upgrade and downgrade heat and supply heat at a suitable temperature level. Such systems are also known as heat transformers and chemical heat pumps (Garg 1985).
- It is feasible to discharge thermochemical systems (e.g., also from room temperature) simply by bringing the reactants together (e.g. opening a valve for gas supply).

The energy is stored in the form of chemical compounds A and B created by an endothermic reaction and it is recovered again by recombining the compounds in an exothermic reaction to compound AB (Equation 5). At high enough temperatures, the products A and B are spatially separated.

$$AB \stackrel{\Delta H_r}{\Leftrightarrow} A + B \tag{5}$$

The heat stored and released is equivalent to the heat (enthalpy) of reaction ΔH_r . The enthalpy of reaction, is often larger than the enthalpy of transition in latent heat storage or the sensible heat stored over a reasonable temperature span. Hence, the storage density, based on solid mass or volume, can be larger for thermochemical storage materials than for latent or sensible heat storage materials. Many thermochemical energy storage concepts are in an earlier stage of development compared to sensible and latent heat systems. In the low-temperature range (<150 °C), thermochemical energy storage is commercially utilized in niche markets (e.g., sorption systems).

The potential of thermochemical storage was identified early in the evolution of CSPtechnology (Ervin 1977, Williams 1978, Brown 1992). A large number of groups actively investigate solar driven chemical processes. These processes aim for solar fuel production and useful chemical products. In a general sense, these approaches also form an energy storage system. In the scope of this chapter, solar driven chemical processes are not further considered.

Thermochemical storage system can be classified into two major categories. **Open type** systems exchange gases with the environment. During the charging process gases are released to the environment. During the discharging process a gas from the environment is utilized. Hence, these systems can operate without gas compression and storage and this simplifies the system design. Gases of interest include oxygen, nitrogen, water vapour and potentially carbon dioxide. Open systems may introduce unwanted substances from the environment. Impurities may be dust, sulphur dioxide, carbon dioxide and organic compounds. Such substances may deteriorate the system performance. System designs with filters may avoid such difficulties. Storage of the unpressurized gas phase in a **closed type system** is usually not feasible because of the unacceptable large gas volume. Commonly, closed type systems compress or condense the gas. Subsequently, the pressurized gas or liquid can be conveniently stored. Alternatively, the gas may be reabsorbed by a second chemical reaction (Sizmann

1980). This discussion indicates that the overall system design rather than a single chemical reaction should be considered.

A **sorption process** can be considered to be a chemical reaction system based on weaker chemical bonds than the covalent bonds encountered in other systems. In a sorption heat storage system, the sorbent is heated during the charging process and vapour is desorbed from the sorbent. During discharging, vapour at a lower temperature is adsorbed (solid sorbent) or absorbed (liquid sorbent) and heat at a higher temperature level can be released. In the low temperature range, <u>adsorption processes</u> using water with materials such as silica gel and zeolites are utilized. Another low temperature option is the <u>absorption reaction</u>. Typical absorption materials for water are MgSO₄, LiCl, LiBr, CaCl₂, MgCl₂, KOH and NaOH (Weber 2008, Beckmann 1984, Zsembinszki 2018). For high temperature applications, sorption systems are typical not considered. Hence, sorption is not discussed further here.

Figure 11 classifies the reversible reactions in three **physical phases**, namely solid-gas, liquid-gas and gas-gas reactions. For the temperature range above 300 °C, mainly solid-gas and to some extend liquid-gas reactions are relevant.



Figure X.11. Classification of thermochemical energy storage by the reaction type.

4.1. Storage materials

Thermochemical storage materials should be characterized by a suitable reaction temperature and enthalpy for the application. Further material requirements are listed in Section 1.1.

Certain solid compounds can undergo **solid-gas reaction** or dissociation reactions when they are heated. A gas is released while the depleted solid remains in the reactor (endothermic reaction, i.e., charging of the store). The parasitic reverse reaction will occur spontaneously if the equilibrium is changed by a temperature decrease or a pressure increase. Therefore, the dissociation products have to be separated and stored individually. For discharge, in the exothermic reaction, the gas is recombined with the solid.

In general there are various types of **solid-gas** reaction systems that can be used for thermochemical energy storage. Among them are the following:

- Dehydration of metal salt hydrates (application in the range of 40 260 °C)
- Dehydration of metal hydroxides (application in the range of 250 600 °C)
- Dehydrogenation of metal hydrides (application in the range of 80 400 °C)
- Decarboxylation of metal carbonates (application in the range of 100 950 °C)
- Thermal desoxygenation of metal oxides (application in the range of 600 1000 °C)

Table 2 shows material systems with a solid-gas reaction of the type $AB_{(s)} \leftrightarrow A_{(s)} + B_{(g)}$, where the subscript (s) defines a solid and (g) is a gas. The table also shows **gas-gas reactions** which usually require a catalyst to obtain high reaction rates. The table shows the equilibrium temperature of the reaction T_r and the heat of reaction related to the educt reactant $\Delta h_{r,educt}$ per mol. Also multiple-step thermochemical cycles, such as the sulphur/sulphuric acid cycles, were examined.

Physical	Material	Material	T_r	$\Delta h_{\rm r,educt}$
phases of	Group		(1 bar)	[kJ/mol]
reaction	_		[°C]	
Solid-gas	Hydroxides	$Ca(OH)_2 \leftrightarrow CaO + H_2O$	505	104
Solid-gas	Ammonium salt	$NH_4HSO_4 \leftrightarrow NH_3 + H_2 + SO_3$	467	337
Solid-gas Salt hydrates		$MgSO_4 \cdot 7H_2O \leftrightarrow MgSO_4 + 7H_2O$	122	411
		$CaCl_2 \cdot 2H_2O \leftrightarrow CaCl_2 \cdot H_2O + H_2O$	174	48
		$CuSO_4 \cdot 5H_2O \leftrightarrow CuSO_4 \cdot H_2O + 4H_2O$	104	226
		$CuSO4 \cdot H_2O \leftrightarrow CuSO_4 + H_2O$	205	73
Solid-gas	Peroxide salts	$BaO_2 \leftrightarrow BaO + \frac{1}{2}O_2$	782	75
		$\mathrm{KO}_2 \leftrightarrow \frac{1}{2} \mathrm{K}_2\mathrm{O} + \frac{3}{4} \mathrm{O}_2$	668	101
Solid-gas	Metal oxides	$6 \operatorname{Mn_2O_3} \leftrightarrow 4 \operatorname{Mn_3O_4} + \operatorname{O_2}$	960	32
		$2 \operatorname{Co}_3 \operatorname{O}_4 \leftrightarrow 6 \operatorname{CoO} + \operatorname{O}_2$	900	200
Solid-gas	Carbonates	$CaCO_3 \leftrightarrow CaO + CO_2$	896	167
		$BaCO_3 \leftrightarrow BaO + CO_2$	1497	212
Solid-gas	Metal hydrides	$MgH_2 \leftrightarrow Mg + H_2$	293	79
		$Mg_2NiH_4 \leftrightarrow Mg_2Ni + 2H_2$	253	128
Gas-gas		$NH_3 \leftrightarrow \frac{1}{2}N_2 + 1.5H_2$	195	49
		$CH_4 + H_2O \leftrightarrow CO + 3H_2$	687	205
		$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	687	247
Hybrid	Sulphur cycle	$\underline{\mathrm{H}}_{2}\underline{\mathrm{SO}}_{4} \leftrightarrow \mathrm{SO}_{3} + \mathrm{H}_{2}\mathrm{O}$	170	132
cycles		$SO_3 \leftrightarrow SO_2 + \frac{1}{2}O_2$	400	99
		$SO_2 + \frac{2}{3}H_2O \rightarrow \frac{2}{3}H_2SO_4 + \frac{1}{3}S$	140	55
		$S + O_2 \rightarrow SO_2$	1250	297

Table 2: Equilibrium temperature and heat of reaction for thermochemical heat storage

4.2. <u>Storage component and heat transfer concepts</u>

Effective thermochemical heat storage reactor design is essential for the effective application of the previously discussed materials. Compared to sensible and latent heat storage, not only heat transfer but in addition mass transfer (e.g. for the gas phase) has to be considered. This fact makes the design of thermochemical reactor design more complex. The reaction may either occur within the storage vessel itself (fixed bed reactor) or the storage material is transported between storage vessel for educts (a separate reactor in which the reaction takes place) and a vessel for the products (moving bed reactors). Examples of solid-gas fixed bed reactors are (Zsembinszki 2018):

- Powder filling
- Substrates with TCS with high-surface area (e.g. honeycombs)
- Composites to improve reaction behaviour or heat transfer
- Fins in the reaction bed to improve heat transfer
- Additional diffusion paths (e.g. pipes) for the gas phase in the reaction zone

Examples of solid-gas moving bed reactors are (Zsembinszki 2018):

- Rotating drum
- Screw reactors
- Fluidised bed reactors
- Gravity-assisted moving bulk reactor

4.3. Storage integration and applications

For **CSP**, several high-temperature thermochemical storage systems have been researched. The dissociation of **calcium hydroxide** (Ca(OH)₂ \leftrightarrow CaO + H₂O) has been investigated and reversibility of the reaction could be proven with a reaction enthalpy of 104 kJ/mol and an equilibrium temperature of 505 °C at 1 bar (Schaube 2010). Fixed bed and gravity-assisted moving bulk reactor in a scale of 10 -100 kWh have been tested at relevant process parameter for integration in a CSP plant with Ranke power cycle (Schmidt 2017).

Solid media sensible heat storage is the classical TES option for CSP central air receivers. As an alternative **metal oxides** thermochemical storage are examined. Several reactor design were studied in lab and small-prototype scale (e.g. rotary drum, fixed bed, gravity-assisted moving bulk reactor) with material systems such as manganese oxide or cobalt oxide (Wong 2010, Stobhe 1999, Agrafiotis 2015, Wokon 2017, Preisner 2019).

Applications in the areas of storage and transportation could utilize gas-gas reactions. The reaction products are transported in a pipeline from the charging source to the consumer with a discharging sink. This system is called chemical heat pipeline or chemical heat pipe (Figure 12).



Figure X.12. Scheme of the simplified principle of a chemical heat pipeline.

For CSP catalysed gas phase reactions for ammonia, sulphur trioxide and methane reforming are of interest (see Table 2). The methane reforming cycle was developed for nuclear application up to 10 MW and is known as the EVA/ADAM process (Tamme 2009). On-sun prototype reactors with a power level of 10 kW to several 100 kW were tested (Lovegrove 2004, Buck 1994). The main drawback of the approach of heterogeneously catalyzed gas

phase reactions in terms of storage is the requirement to separate, compress and store gases thus adding to the cost and complexity of the process.

This disadvantage can be overcome by additional reaction steps as for the **sulphur based cycle** with multiple reactions (see Table 2) (Müller 2000a, Müller 2000b, Wong 2015). The cycle consists of on-sun sulphuric acid evaporation and decomposition, the sulphur dioxide disproportionation and the efficient sulphur combustion (Norman 1982a, Norman 1982b, Harman 1977, Wong 2015). Several prototype reactors for the different reaction steps have been tested (Prieto 2016). Large-scale experience of many components of this cycle exists from sulphuric acid plants. The storage capacity of this cycle originates from sulphuric acid and sulphur storage volumes. In addition also other cycles for hydrogen production, such as the sulphur-iodine cycle (Goldstein 2005) and the Westinghouse cycle (Guerra Niehoff 2015) are examined.

5. Summary and conclusion

This chapter gave some background and principles of thermal energy storage (TES) by sensible heat storage in liquids and solids, phase change materials and thermochemical storage. The chapter structure followed the value chain of TES development from material, via component to system integration research and development. The largest amount of work on TES focuses on low-temperatures rather than ultra-high temperatures (e.g. >800 °C) as considered in this book.

For example *sensible* heat storage in liquids became commercially available in the form of molten salt storage for concentrating solar power (CSP) up to 400 °C in 2008 (Andasol plants in Spain) and up to 560 °C in 2011 (Gemasolar in Spain). At the time of writing, beyond 560 °C there is no liquid TES system commercially available. This is also due to the situation that hydraulic components such pumps and valves at elevated temperatures are rare. Hence, utilization of liquids for ultra-high temperature requires further research for material qualification (e.g. corrosion), process technology (purity control for liquid and gas phase) and component development for advances in this field.

The situation for **sensible heat storage in solids** is different. Regenerator type storage systems for gases as heat transfer fluid are commercially available since more than 120 years. Still today, large-scale systems are installed in the glass, as well as in the iron and steel industry. Hot temperatures up to 1400 °C can be released. Hence, sensible heat storage in solids can be considered a viable solution for ultra-high temperatures. Hence, the research and development should aim for adapted and optimized solutions, as well as system integration aspect for individual applications.

The use of latent heat storage in **phase change materials** (PCM) in the form of water/ice as seasonal storage is old. Also today, ice-storage is widely used in modern commercial buildings for cooling. Systematic scientific examinations on PCMs started around 1960 with space research programs (Lane 1983). Nowadays the commercial utilization of PCM with melting temperatures below 100 °C in mainly limited to several commercial niche markets. The pocket warmer invented around 1930 is one prominent example. PCM storage for high-pressure steam in the temperature (pressure) range 180 °C (10 bar) to 340 °C (150 bar) is in a pre-commercial phase with full-scale prototypes being tested in the application environment. Research on PCM for ultra-high temperatures (> 800°C) is very limited and the work is mainly on a material level with the selection of suitable PCMs (e.g. metals, alloys, salts) and compatible container materials rather than on TES component or system integration aspects. For ultra-high temperatures, research could focus on applications with a narrow operation window of the TES and the demand of high energy densities.

At the time of writing, **thermochemical storage** solutions are limited to commercial niche markets mostly with a specific benefit of the thermochemical reaction. Specific benefits compared to sensible and latent heat storage include a typically high energy density, the long-term storage at room temperature with a simple start for heat generation, as well as the capability to operate in different heat pump modes. Literature indicates that systematic research on high-temperature thermochemical storage for CSP started around 1970 (Wenthworth 1976). On a component and system integration level thermochemical storage are more complex compared sensible and latent heat storage. This is due to the fact that not only heat transfer occurs but also mass transfer due to the separation of educt and product has to be taken into account. It seems likely that thermochemical research effort is fruitful in areas where the specific benefits justify the higher complexity of thermochemical storage.

It is the hope of the author that the overview in this chapter inspires the research and development on improved and new solutions for ultra-high temperature thermal energy storage, transfer and conversion in future.

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