Assessment of thermal energy storage options in a sodium-based CSP plant

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HIGHLIGHTS

- Evaluation of thermal energy storage systems for sodium-based central receiver.
- Sensible, latent and thermochemical systems are compared.
- One tank sensible system and thermochemical systems most promising solutions.

Sodium has proven to be an efficient heat transport fluid in a central receiver system in the IEA-SSPS facility in Almeria in the 1980s with a 5 $\mathrm{MWh_{th}}$ direct two tank storage system. In recent years the interest in liquid metals, particularly sodium, as heat transfer fluids for concentrating solar power has reawakened. However, an assessment of thermal energy storage options in a liquid metal-based concentrating solar power system has not been performed yet. In this paper sensible, latent and thermochemical systems, described in the literature and potentially suitable for a solar power plant using sodium, are investigated. As sensible systems, direct sodium two tank and one tank thermocline storage systems with filler are considered, as well as indirect molten salt systems. Latent systems include configurations with finned tubes, packed beds of phase change material capsules and active screw type systems. In addition, metal hydride dehydrogenation, ammonia dissociation and hydroxide dehydration are considered as thermochemical storage systems. The presented storage systems are discussed and compared on the basis of the following criteria: Storage medium cost, storage density, cycling behaviour, maturity level and suitability for sodium as heat transfer fluid. As a result, the direct sodium thermocline one tank storage with filler material represents a promising direct storage option. It could be further enhanced by a cascaded arrangement of phase change capsules. Moreover, the thermochemical storage systems based on ammonia dissociation or hydroxide dehydration are identified as best indirect storage options.

1. Introduction

Within the renewable energy technologies the solar thermal electricity (STE) or concentrating solar power (CSP) is of particular interest due to the applicability of a thermal energy storage (TES) system which enables dispatchibility in energy supply, as the CSP plant can react to the electricity demand and even supply electricity after sunset. In addition, the capacity factor of the power plant can be significantly increased with a TES system. Current operational solar tower power plants work with water/steam or molten salt as heat transfer fluids (HTF). High storage capacities up to 15 h (Gemasolar) can only be achieved with molten salt two tank technology at the moment [1]. The commercially used solar salt is a binary mixture of 60% $NaNO_3$ and 40% KNO_3. However, the operation with molten salt is currently limited to 290 °C and 565 °C, defined by the melting and the chemical decomposition temperature [2]. Liquid metals (LM) are a promising alternative due to their high boiling temperatures and excellent heat transfer characteristics [3]. Sodium, tin, lead-bismuth eutectic and also sodium–potassium are proposed as main candidates, as they also show relatively low melting points [4,5]. Among these, sodium possesses the best heat transfer characteristics, but presents a safety risk due to the high reactivity with humid air or water. It has already been tested as heat transfer fluid in a central receiver system in the IEA-SSPS in Almeria in the 1980s

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Nomenclature

Acronyms

CSP	concentrating solar power
HTF	heat transfer fluid
HX	heat exchanger
LM	liquid metal
PCM	phase change material
STE	solar thermal electricity
TES	thermal energy storage system

Greek symbols

ϵ	void fraction (–)
ρ	density (kg m^{-3})

Latin symbols

c_p	heat capacity (J kg^{-1} K^{-1})
C	storage capacity (J kg^{-1}) or (J m^{-3})
h	enthalphy (J kg^{-1})
m	mass (kg)
p	pressure (Pa)
Q	thermal energy (J)
T	temperature (°C)
V	volume (m^3)

Subscripts

l	liquid
m	mass specific
melt	melting
reac	reaction
s	solid
V	volume specific

[6] with a storage system of 5 MWh_{th} [7] and regained interest in recent years [8–10].

Thermal energy storage in a sodium-based central receiver system beyond the two tank arrangement used in the IEA-SSPS has not been investigated yet in recent literature, even though it is crucial for the competitiveness of a LM-based CSP system with respect to the state-of-the-art molten salt technology. Particularly alternative storage options like latent and thermochemical storage have not been evaluated systematically in combination with sodium as HTF.

On the basis of selected criteria (Section 2) possible long term storage options (Section 3) for a large scale sodium-based solar tower system are discussed. As a result, the most promising storage options are determined and research gaps are pointed out (Section 4).

2. Evaluation criteria

The selected criteria are supported by data from cited literature and complemented by own calculations with specified equations. If data is missing for a quantitative assessment, only a qualitative evaluation is performed. The criteria are chosen in accordance with [1,11].

- *Storage medium cost*: Only the investment cost for the raw storage material is considered in this paper.
- *Storage density*: Both the mass and volume specific storage density of the selected storage materials are compared to the reference molten salt. The mass specific storage density directly influences the storage material cost that results for a certain storage capacity. However, the volume specific density is linked to the tank size required and therefore tank material and insulation cost.
- *Cycling behaviour*: This criterion reflects on the performance during the charging and discharging cycles and describes the challenges that need to be met to achieve a reversible process. Besides, it is assessed, if constant outlet temperatures can be reached.
- *Maturity level*: The maturity of the storage technologies is estimated from lab scale experiments up to commercial applications.
- *Suitability for sodium*: This criterion examines the applicability of sodium for the proposed storage systems and the compatibility with filler, heat exchanger (HX) and tank material. Furthermore, possible risks are estimated.

Altogether, the selected criteria shall enable to draw a conclusion on the advantages and disadvantages of using sodium regarding each presented storage system and indicate the research gaps that need to be filled in the future.

3. Systems

In this paper sensible, latent, combined sensible-latent and thermochemical storage systems are proposed and discussed. The considered storage systems are listed in Table 1 and described in detail in the following subsections.

3.1. Sensible

Thermal energy can be stored by heating a solid or liquid material and successively released by cooling it down (Eq. (1)).

$$Q_{sens} = c_p \cdot \rho \cdot V \cdot \Delta T \tag{1}$$

The thermal capacity per unit volume ($c_p \cdot \rho$) of the storage medium is crucial for the amount of energy that can be stored in a material for a given volume and temperature difference [12]. The sensible thermal energy can be stored directly or indirectly. In a direct sensible storage the HTF acts at the same time as the

Table 1
List of considered storage systems.

System	Description	Results
Sensible	3.1	4.1
Direct two tank sodium	3.1.1	
Direct one tank sodium	3.1.2	
Indirect two tank molten salt	3.1.3	
Indirect one tank molten salt	3.1.4	
Indirect with gas as HTF and solid storage	3.1.5	
Latent	3.2	4.2
Finned tubes	3.2.1	
Packed bed PCM	3.2.2	
Screw type	3.2.3	
Combined sensible-latent	3.3	4.3
One tank thermocline with PCM	3.3.1	
Composite material	3.3.2	
Gas as HTF with combined sensible-latent storage	3.3.3	
Thermochemical	3.4	4.4
Metal/metal hydride	3.4.1	
Ammonia/nitrogen/hydrogen	3.4.2	
Calcium hydroxide/calcium oxide	3.4.3	

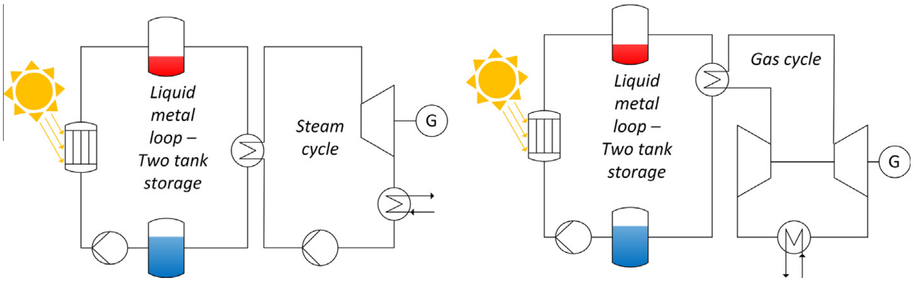

Fig. 1. Direct two tank sodium system; left: Rankine steam cycle; right: Brayton gas cycle.

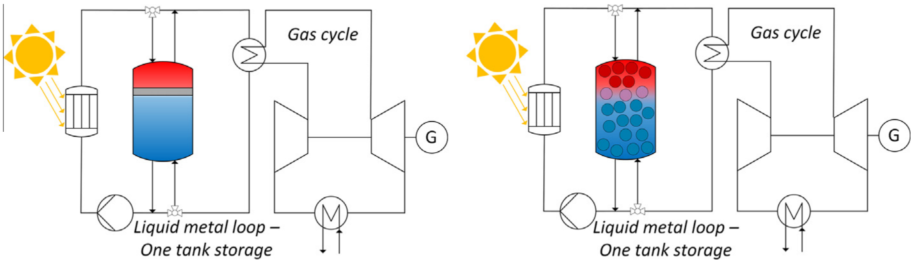

Fig. 2. Direct one tank sodium system; left: floating barrier; right: packed bed thermocline.

storage medium. In an indirect storage system, the heat is transferred from the HTF to a second medium which acts as the storage medium.

Three direct concepts are described in this section, followed by three indirect concepts.

3.1.1. *Direct two tank sodium*

The direct two tank system with molten salt is the most advanced storage system and is already used in commercial solar tower power plants [1]. This concept has already been tested with sodium as HTF [7]. The higher temperatures that can in principle be achieved with sodium allow for a supercritical steam cycle or a gas cycle to be used for power generation (Fig. 1).

3.1.2. *Direct one tank sodium*

To reduce the cost of the tank material, the storage material can be stored in only one tank with an upper hot and a bottom cold part [13]. Those can be separated by a floating barrier that is lifted and lowered during discharging and charging (Fig. 2 left). Another option is to replace parts of the storage medium by solid filler material, the hot part of the fluid is separated by a thermocline from the cold part (Fig. 2 right).

3.1.3. *Indirect two tank molten salt*

The indirect two tank storage system with molten salt is commercially used in parabolic trough power plants with thermal oil as HTF [14]. An indirect two tank system with molten salt could also be applied for sodium as HTF (Fig. 3).

3.1.4. *Indirect one tank molten salt*

In analogy with Section 3.1.2 a one tank molten salt system with filler material (or floating barrier) could be used (Fig. 4).

3.1.5. *Indirect with gas as HTF and solid storage*

Another possibility of indirect storage uses a secondary HTF (gas) to transfer the thermal energy to a solid storage (Fig. 5) [15]. The same gas could be used for heating up the solid storage as well as for the gas cycle [16]. In particle receiver systems, moving bed HX are developed with particles flowing through tubes on one side and gas or steam being heated up on the other side [17,18].

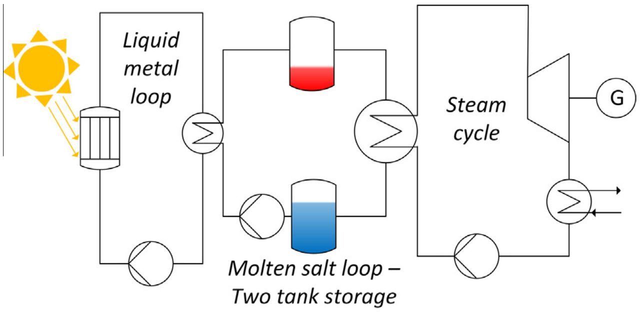

Fig. 3. Indirect two tank molten salt system.

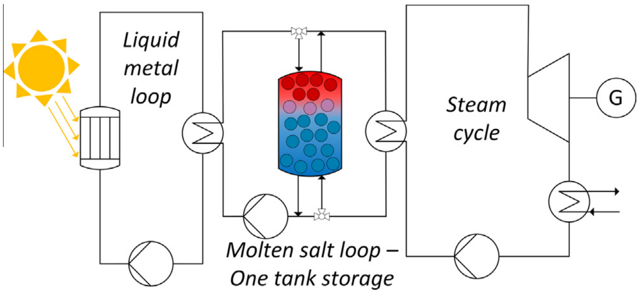

Fig. 4. Indirect one tank molten salt system.

3.2. *Latent*

Mainly solid–liquid phase change is considered for latent thermal energy storage in the literature [12]. The melting enthalpy Δh_{melt} in the charging process can be released during the discharge process, when the phase change material (PCM) solidifies again (Eq. (2)).

$$Q_{\mathrm{lat}} = m \cdot \Delta h_{\mathrm{melt,m}} \tag{2}$$

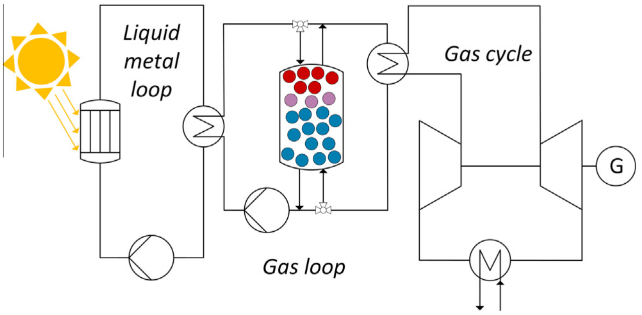

Fig. 5. Indirect with gas as HTF and solid storage system.

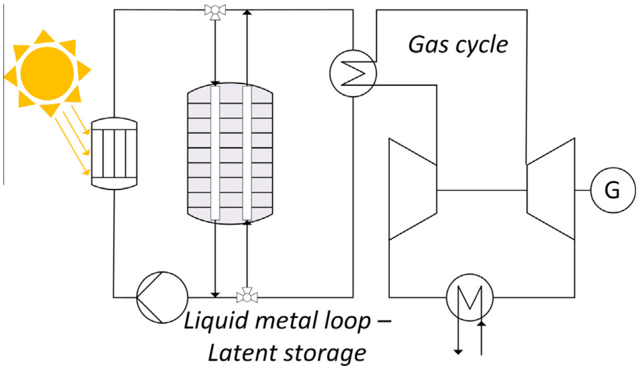

Fig. 6. Finned tubes system.

During the discharging process the solid front moves away from the heat transfer surface and the thermal resistance in this growing layer penalizes the heat transfer [19]. Therefore methods have been developed to minimize this influence: (a) by increasing the heat transfer surface or (b) by moving the PCM through the HX to free the surface from solid material. Furthermore, cascaded storages with decreasing melting temperatures in charging direction are proposed in order to reach a higher exergetic efficiency due to an optimal utilization of the PCM [20].

3.2.1. Finned tubes

In this concept the HX surface is increased by using finned tubes (Fig. 6) [21]. The liquid metal flows through the tubes and the heat is transferred to a PCM which melts during charge and solidifies during discharge.

3.2.2. Packed bed PCM

The packed bed PCM system is similar to a one tank system with filler (Section 3.1.2). However, the filler is an encapsulated PCM (Fig. 7) [22]. To achieve thermal stratification in the tank several PCM with decreasing melting temperatures can be used in a cascaded storage [20].

3.2.3. Screw type

In a screw type storage the PCM is moved by a screw HX from a cold solid to a hot liquid tank, as illustrated in Fig. 8 [23]. This concept is comparable to an indirect two tank system.

3.3. Combined sensible-latent

In this storage concept part of the sensible storage medium is replaced by PCM to increase the storage density [24]. Additionally, the charging and discharging rates can be significantly increased compared to a latent concept only, where the relatively low thermal conductivities of the PCM lead to low loading and unloading times [25]. In practice this means some filler material in a packed bed is replaced by PCM capsules or PCM is inserted in foams or other solid structures.

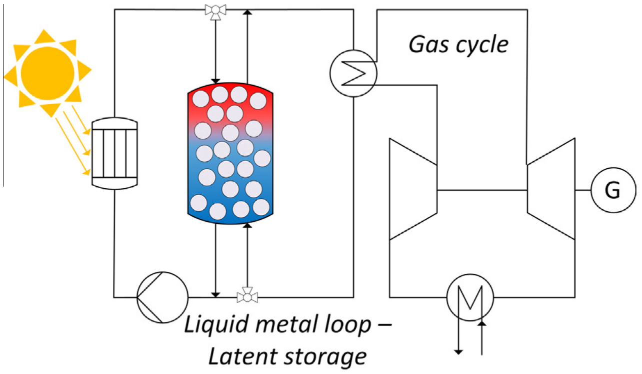

Fig. 7. Packed bed PCM system.

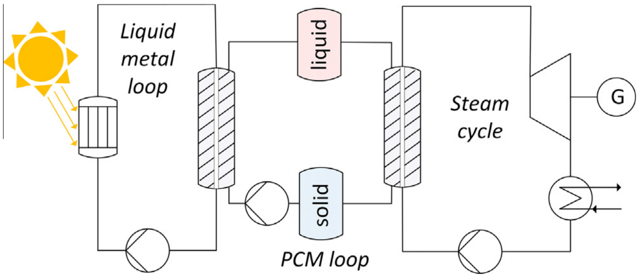

Fig. 8. Screw type system.

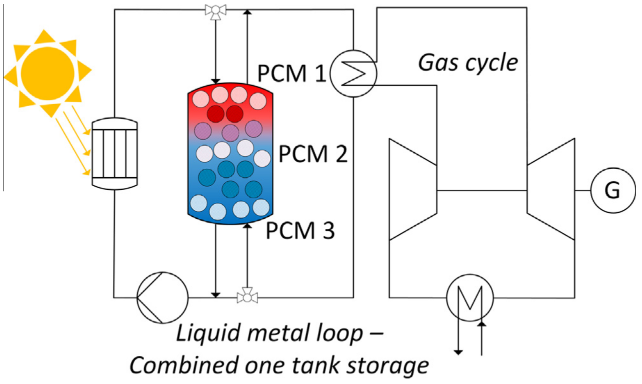

Fig. 9. Combined one tank thermocline system.

3.3.1. One tank thermocline with PCM

The combined one tank thermocline is filled with alternating layers of PCM capsules and solid filler material [26]. The PCM material with the highest melting temperature is on top of the tank where the hot HTF enters. At the bottom of the tank the PCM with the lowest melting temperature ensures that the HTF leaves the tank with its desired outlet temperature (Fig. 9).

3.3.2. Composite material

Another possibility is to utilize a composite material (e.g. foams) consisting of a highly conductive solid sensible storage medium and a PCM with a high storage capacity, e.g. graphite and eutectic salt [25]. In other concepts the PCM is encapsulated

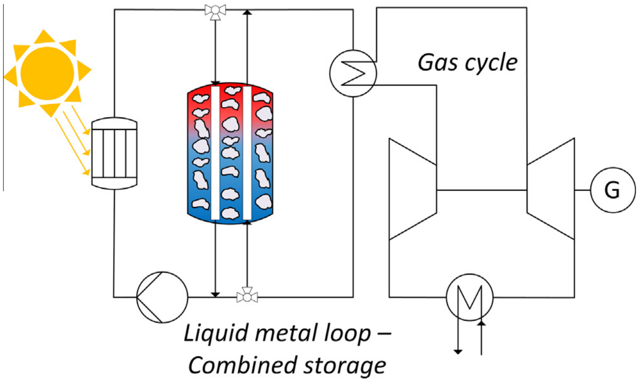

Fig. 10. Composite material storage system.

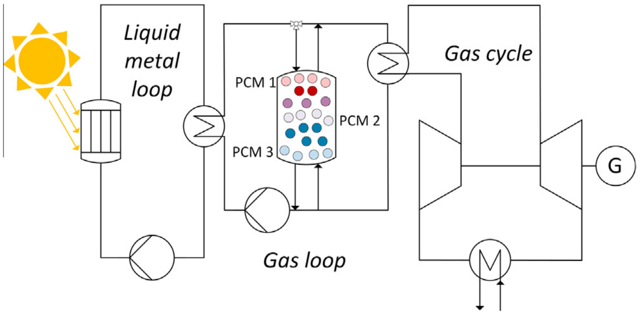

Fig. 11. Gas as HTF with combined sensible-latent storage system.

in tubes and inserted into holes in the solid storage material [27]. Sodium flows through tubes, as illustrated in Fig. 10, and the heat is transferred to the material similar to the finned tubes concept.

3.3.3. *Gas as HTF with combined sensible-latent storage*

The combined sensible and latent storage system can also be heated up by a secondary HTF. The gas could be in direct contact with the storage material (see Fig. 11).

3.4. *Thermochemical*

A thermochemical storage system utilizes the thermal energy that is released in an exothermic reaction during the discharging process according to Eq. (3). In the charging process the endothermal reaction takes place (shift to left) [28].

$$Educts \leftrightarrow Products + Q_{\mathrm{reac}} \tag{3}$$

Various reactions are proposed in the literature [12,29]. In this section three thermochemical storage options that are most promising for the pursued working temperatures of 600 °C and above are presented. Similar to the cascaded latent storage systems different thermochemical storage systems with decreasing reaction temperature in charging direction can be used in a cascaded storage [30].

3.4.1. *Metal/metal hydride – hydrogenation/dehydrogenation*

In case thermal energy is abundant the high temperature metal hydride (HTMH) is charged. Hydrogen is released and can be stored directly [31] or in a low temperature metal hydride (LTMH), where heat is released at a low temperature and extracted [32]. For the discharging process these reactions can be reversed as illustrated in Fig. 12. Paskevicius et al. [31] and Corgnale et al. [32] listed metal dehydrogenation temperatures from 200 °C to 1200 °C.

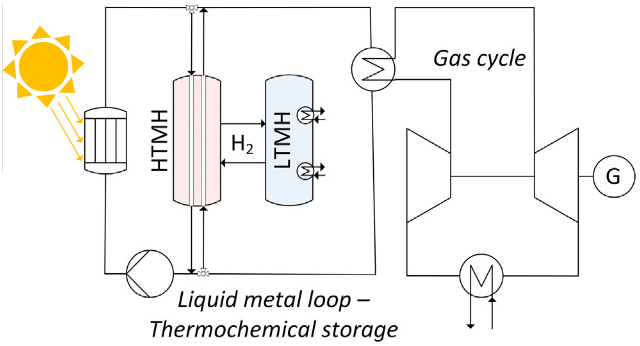

Fig. 12. Metal/metal hydride system, adapted from [32].

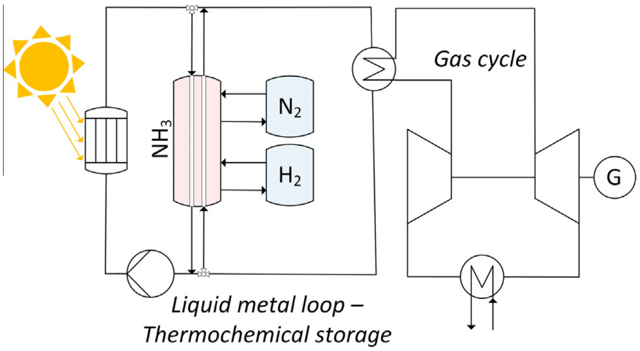

Fig. 13. Ammonia/nitrogen/hydrogen system.

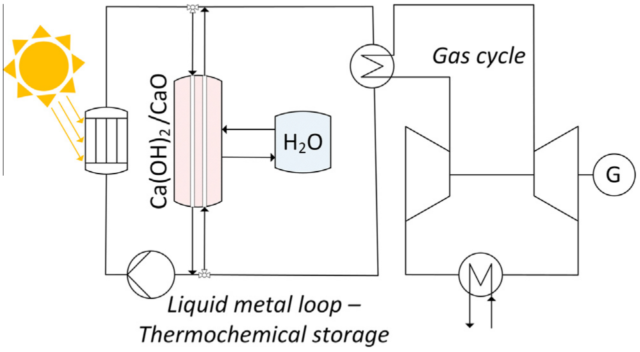

Fig. 14. Calcium hydroxide/calcium oxide system.

3.4.2. *Ammonia/nitrogen/hydrogen – dissociation/synthesis*

This storage system benefits from the long lasting experience with the *Haber Bosch* process. Ammonia is dissociated at high temperature and pressure (at 700–800 °C and 20 MPa) to N_2 and H_2. The gases can be stored at ambient temperature until they are used for the reverse reaction (Fig. 13) [33].

3.4.3. *Calcium hydroxide/calcium oxide – dehydration/hydration*

During the endothermal process $Ca(OH)_2$ reacts to CaO and water, whereas the water vapour is condensed and then stored in liquid state (Fig. 14) [34]. A stable cycle was demonstrated up to 410 °C [34], but according to Pardo et al. [29] temperatures up to 900 °C are possible in principle with a low pressure of 0–0.2 MPa.

4. Results

4.1. *Sensible storage systems*

The sensible storage options are compared with respect to the criteria listed in Section 2. The state-of-the-art two tank molten salt system is taken as reference for the evaluation.

Table 2
Physical properties and cost data of storage materials for sensible storage.

Medium	$c_{p,m}$ (kJ kg^{-1} K^{-1})	$c_{p,V}$ (MJ m^{-3} K^{-1})	ρ (kg m^{-3})	cost$_i$ (€ kg^{-1})	Ref.
Molten salt	1.55	2.95	1903	1.0	[8,40]
Sodium	1.25	1.01	808	2.6	[8,40]
Quartzite	1.2	3.18	2651	0.5	[8]

4.1.1. Storage medium cost

The investment costs for the complete storage system should not exceed 15 €/kWh$_{th}$, according to the Strategic Research Agenda 2020–2025 [35], or 15 \$/kWh$_{th}$, stated by the Sunshot Initiative of the US Department of Energy [36].

Reilly and Kolb [37] summarized the costs for the Solar Two plant and calculated investment costs of 30 \$/kWh$_{th}$ for the molten salt two tank storage. For an indirect two tank system, as it is installed in parabolic trough plants, Kelly and Kearney [14] calculated half of the investment costs for the storage medium and overall costs for the entire storage system including HX, tanks, pumps and instrumentation of 30 €/kWh$_{th}$.

Pacheco et al. [38] compared the cost of an indirect one tank molten salt storage with quartzite filler with an indirect two tank molten salt system. The investment costs for a system's capacity of 688 MWh are 20 \$/kWh$_{th}$ and 31 \$/kWh$_{th}$ respectively and include the costs for storage medium, tank and HX. This shows that a cost reduction of 30% is possible by avoiding the second tank and replacing the storage medium partly by a low cost filler material. According to [38], the storage medium represents 56% of the investment costs for the two tank and 43% for the one tank system. A similar study was carried out by Strasser and Selvam [39] for a one tank molten salt storage with limestone as filler material and a structured thermocline system with concrete for a capacity of 2165 MWh. They evaluated investment costs of 30 \$/kWh$_{th}$ (with 14% storage medium cost) and 34 \$/kWh$_{th}$ (with 18% storage medium cost). Also included in the investment costs are insulation, tanks, piping, construction costs, contingency, engineering costs and sales tax. This could explain why the investment costs are in the same range as a two tank molten salt system and not 30% lower as in the calculation done by Pacheco [38].

This data shows that an estimation of the storage cost depends strongly on the materials used, on the capacity of the CSP plant and on the components included in the calculation. A thorough economic analysis is therefore always system-dependent. In this paper, however, only the storage medium costs are considered, as the aim is a prelimary selection of promising storage options and not a detailed system analysis.

The storage medium cost in €/kWh of a dual-media storage are calculated with Eq. (4) using the physical properties and cost data of Table 2 (l = liquid, s = solid). The void fraction ϵ is set to 0.25, similar to [8,41]. In a review of Singh et al. [42] void fractions of 0.136 to 0.67 are listed depending on the storage material.

$$\text{cost}_{\text{dual-media}} = \frac{\rho_l \cdot \epsilon \cdot \text{cost}_l + \rho_s \cdot (1-\epsilon) \cdot \text{cost}_s}{\Delta T \cdot (\epsilon \cdot \rho_l \cdot c_{p,l} + (1-\epsilon) \cdot \rho_s \cdot c_{p,s})} \tag{4}$$

For a single-medium storage the calculation simplifies to Eq. (5):

$$\text{cost}_{\text{single-medium}} = \frac{\text{cost}_l}{\Delta T \cdot c_{p,l}} \tag{5}$$

The results are summarized in Table 3. It has to be noted, that the price of the storage media is dependent on demand and supply and can therefore differ from the given values. The storage medium cost per kWh are strongly dependent on the temperature difference between charging and discharging. These temperatures result from the power block that is applied. In all currently operational commercial CSP plants steam turbines (Rankine cycle) are used (up to 550 °C in case of superheated steam). In research projects also gas turbines (Brayton cycle) are applied, which enable higher temperatures to be utilized [1]. In operating solar tower systems, the lower and upper temperatures of the molten salt storage are 290 °C and 565 °C. Therefore these limits are taken for a first comparison of storage medium cost. As can be seen in Table 3, a single-medium sodium storage would be more than three times as expensive as a molten salt one for an upper temperature of 565 °C. The addition of a filler material leads to a reduction of the storage medium cost in general and to an alignment of the storage medium cost for molten salt and sodium.

Table 3
Cost and storage density of storage medium with and without filler (quartzite) with varying upper operating temperatures.

Medium	T_{min} (°C)	T_{max} (°C)	C_m (kJ kg^{-1})	C_V (MJ m^{-3})	cost (€ kW^{-1} h^{-1})
Molten salt	290	565	426.3	811.2	8.4
Sodium (a)	290	565	343.8	277.8	27.2
Sodium (b)	290	640	437.5	353.5	21.4
Molten salt with filler	290	565	348.6	858.9	6.2
Sodium with filler (a)	290	565	331.3	725.6	7.5
Sodium with filler (b)	290	640	421.6	923.4	5.9

As already mentioned, the upper temperature of molten salt is limited to its decomposition temperature. However, higher temperatures are possible with sodium in principle. The upper temperature limit of sodium is 883 °C (boiling temperature) [40], but for a first assessment an upper temperature of 640 °C is assumed, similar to [8]. This could be in principle realized in an ultra-supercritical steam or a gas cycle. With this higher upper temperature of 640 °C a dual-media sodium storage with filler has the lowest storage medium cost compared to the other sensible liquid storage systems, both single-medium and dual-media. With a gas cycle even higher temperatures and therefore further storage medium cost (in €/kWh) reduction could be achieved for a sodium storage in principle.

It has to be noted, that these values are estimated with a void fraction of $\epsilon = 0.25$, for void fractions higher than $\epsilon > 0.3$ the storage medium cost of a dual-media molten salt storage starts to be lower than for the dual-media sodium storage ($T_{upper} = 640$ °C).

For a solid storage with a secondary HTF (see Section 3.1.5) Steinmann et al. estimated 13% for the storage medium (3.9–4.6 €/kWh$_{th}$), but 57% for the HX [15]. However, this basalt storage system is only tested up to 390 °C yet [43]. Experimental work with concrete composites show the feasibility of such a storage system up to 600 °C [44,45].

4.1.2. Storage density

The specific mass and volumetric heat capacities of the storage materials are presented in Table 2. Molten salt has a higher mass heat capacity than sodium and the filler material. Due to its high density, the volumetric heat capacity of molten salt is more than twice as large as that of sodium. By adding the filler material the mass specific heat capacities of the liquid storage materials are reduced (20% for molten salt and 4% for sodium) and the volumetric heat capacities of the storage materials are increased, with a much larger effect on sodium (6% for molten salt and 160% for sodium). The values are again calculated for a void fraction of $\epsilon = 0.25$ and displayed in Table 3. The storage densities in Table 3 in kJ/kg and kJ/m^3 are calculated for the given temperature differences to compare the storage densities of single- and dual-media storages and to evaluate the influence of an increased upper temperature according to Eqs. (6)–(9).

$$C_{\text{single-medium,m}} = c_{\text{p,i}} \cdot \Delta T \tag{6}$$

$$C_{\text{dual-media,m}} = \frac{c_{\text{p,l}} \cdot \rho_{\text{l}} \cdot \epsilon + c_{\text{p,s}} \cdot \rho_{\text{s}} \cdot (1-\epsilon)}{\rho_{\text{l}} \cdot \epsilon + \rho_{\text{s}} \cdot (1-\epsilon)} \cdot \Delta T \tag{7}$$

$$C_{\text{single-medium,V}} = C_{\text{single-medium,m}} \cdot \rho_{\text{l}} \tag{8}$$

$$C_{\text{dual-media,V}} = C_{\text{dual-media,m}} \cdot (\epsilon \cdot \rho_{\text{l}} + (1-\epsilon) \cdot \rho_{\text{s}}) \tag{9}$$

The mass density is an important parameter for the assessement of storage systems, because it is related to the storage medium cost per kWh_{th} and to the distributed load on the foundation. The costs for the storage tank and the insulation, however, are dependent on the volumetric density of the storage. The higher the volumetric density, the smaller the storage tank can be and as a result lesser material is needed for the tank and insulation. A large volume could in the worst case lead to splitting the large tank into two or more smaller tanks, which would again increase the investment costs for the tank, piping and pumping. The mass and volume storage density of a dual-media tank is higher for molten salt than for sodium for the same temperature difference. However, sodium can be heated up to higher temperatures and for an upper temperature of 640 °C both mass and volumetric storage density are higher for a dual-tank with sodium. Additionally, it has to be noted that part of the storage volume in a dual-media storage (20–30%) cannot be utilized due to the thermocline between the hot and cold part which has to be maintained [1].

4.1.3. Cycling behaviour

The cycling behaviour of the molten salt two tank systems is well-known in operational solar tower and parabolic trough plants. The cycling behaviour of thermocline storages is tested on pilot scale and no significant deterioration of the filler material has been observed [38,51]. However, one problem that can occur in thermocline storages is thermal ratcheting. Thermal ratcheting describes the occurance of different dilation of the tank and the filler material during cycling, which can lead to deformation and cracks [52]. Furthermore, during charging and discharging the thermocline layer is lowered and lifted in the storage tank and needs to remain stable to prevent mixing of hot and cold fluid. For the solid storages with gas as a secondary HTF, good cycling behaviour has been demonstrated for concrete in a temperature range between 300 °C and 400 °C [44]. John et al. [45] confirmed the stability of concrete mixtures for higher temperatures up to 600 °C on lab scale. The charging and discharging flow of the hot and cold gas needs to be carefully controlled, as a stable outlet temperature is difficult to achieve as the solid medium cools down while being discharged [43].

4.1.4. Maturity level

The two tank molten salt storage is the best-developed system and is used in commercial CSP plants, e.g. 2300 MWh_{th} storage in Gemasolar [53]. In the IEA-SSPS test facility also a two tank sodium system with 5 MW_{th} has already been used as storage [6]. Thermocline molten salt systems as well as solid storages are tested on pilot scale [51,54]. For liquid metals no such tests have been carried out to the knowledge of the authors.

4.1.5. Suitability for sodium

The main advantage of a direct sodium storage is the possibility to go to higher temperatures than molten salt and that no HX to a secondary storage fluid is required. However, the tank and the piping have to be welded and airtight to avoid a risk of a sodium reaction with humid air. In a dual-media storage the filler material has to be absolutely water free so that there is no possibility that sodium can react. In indirect concepts there is the risk of a reaction of sodium with molten salt if there is a leakage in the HX. On the other hand, for the direct storage a leakage in the HX to the steam cycle is also a non-negligible risk.

As promising as the dual-media storage is from the cost and storage density point of view, it is possible that a thermal stratification in the tank, in order to separate the cold from the hot fluid, cannot be realized due to the large thermal conductivity of sodium. Research should be done on this subject in order to determine the general feasibility and to define the optimum parameters for such a storage with sodium (void fraction, solid particle diameter, aspect ratio, etc.).

The main advantages and disadvantages of the possible sensible storage systems are summarized in Table 4. The evaluation of the proposed sensible storages shows that compared to the state-of-the-art system (two tank molten salt) all systems have a lower maturity level. The costs for a one tank storage with sodium and

Table 4
Summary of evaluation of sensible storage concepts.

Concept	Advantages	Disadvantages
Sensible in general	+ Mature system: two tank molten salt is state-of-the-art in operating CSP facilities	– Low storage densities
Two tank sodium	+ Simple system + Constant HTF output temperature during discharge + Well-tested cycling behaviour of two tank system + Operational experience in IEA-SSPS in Almeria	– Limited potential for further cost reduction – Risk of sodium reaction in HX to steam cycle in case of leakage – High potential damage due to large amount of sodium
One tank sodium	+ Cost reduction by partial replacement of storage medium and only one tank possible + Practical experience on pilot scale with oil and molten salt + Minimized potential damage as amount of sodium is reduced	– Compatible filler material required – Reduced storage capacity due to thermocline – Complex cycling – Risk of sodium reaction in HX to steam cycle in case of leakage
Two tank molten salt	+ Simple system + Experience in operating CSP facilities (highest maturity level)	– Limited operating temperature – Risk of sodium reaction in HX to molten salt cycle in case of leakage
One tank molten salt thermocline	+ Cost reduction by partial replacement of storage medium and reduction to one tank possible + Practical experience on pilot scale	– See two tank molten salt – Compatible filler material required – Reduced storage capacity due to thermocline – Complex cycling
Gas as HTF and solid storage	+ Low cost storage material	– High cost HX – Temperature decrease during discharge as solid medium cools down

Table 5
Physical properties and cost data of selected PCM: salts, salt eutectics, metals and metal alloys.

Medium	T_{melt} (°C)	ρ (kg m^{-3})	$\Delta h_{\text{melt,m}}$ (kJ kg^{-1})	$\Delta h_{\text{melt,V}}$ (MJ m^{-3})	cost_i (€ kg^{-1})	cost (€ kW^{-1} h^{-1})	Ref.
Al	660	2700	397	1072	n.a	n.a.	[46]
56%Cu/27%Si/Mg	770	1900	420	798	n.a.	n.a.	[46]
NaCl	802	2160	520	1123	0.1	1.2	[47]
67% NaF/MgF_2	832	2140	616	1318	n.a.	n.a.	[48]
LiF	845	2640	1044	2756	5.38	18.6	[48,49]
Li	849	534	1041	556	n.a.	n.a.	[48]
Na_2CO_3	854	2530	276	698	0.2	2.6	[47,50]
K_2CO_3	897	2290	236	540	0.6	9.1	[50]

filler are comparable to molten salt systems. Furthermore it has to be noted that only medium costs are taken into account in this cost estimation. Tank material, HX, pumps, piping, etc. are left out. For sodium completely airtight tanks and piping has to be installed compared to molten salt, which could lead to higher costs for these components.

4.2. Latent storage systems

For desired melting temperatures of 600 °C and above selected PCM are presented in this section. Depending on the storage type, the PCM is either used as bulk material or as capsules, a list of suitable materials can be found in [48,49,55,56].

4.2.1. Storage medium cost

In latent thermal energy storage systems large heat transfer areas are necessary. The finned tubes concept is the easiest way to increase the heat transfer area; encapsulation and screw type are more complicated concepts and therefore possibly more expensive. A cost estimation of a shell-and-tube latent storage by Bai et al. [57] showed that with a low cost PCM material the storage system can be competitive with a two tank system in the future. Nithyanandam et al. [58] conducted a cost and performance analysis of a CSP system with an included latent heat storage. They compared the costs of both encapsulated PCM storage and a latent heat storage with embedded heat pipes with the target of 15 $/$kWh_{th}$ set by the SunShot Initiative [36]. With the optimal capsule radius and the optimal space between the heat pipes the costs targets could be met. A cost analysis by Robak et al. [59] of a latent storage with embedded heat pipes was executed for a large scale CSP plant with the result that the capital cost could be decreased by 15% compared to a sensible two tank system. The storage medium costs of suitable PCM with melting temperatures higher than 600 °C are listed in Table 5, not included are further costs for encapsulation. Material cost data scatter in a wide range from 0.1 to 5.38 €/kg and 1.2 to 18.6 €/kWh_{th} and there is a general lack of validated cost data in the literature.

4.2.2. Storage density

The storage density can be significantly higher than in sensible concepts due to the utilized melting enthalphy. Kotzé [5] stated that metals possess latent heat capacities up to 500 kJ/kg and fluoride salts even up to 900 kJ/kg. In Table 5 the melting enthalpies related to mass and volume of selected PCMs are listed. It is recognisable that the melting enthalphies of chloride and fluoride salts and aluminium lead to higher mass and volume specific storage densities compared to molten salt (see Table 3). Regarding the storage density, these materials overrule an indirect molten salt two tank storage.

4.2.3. Cycling behaviour

The thermal resistance due to lower heat transfer in solid PCM during discharge hinders a smooth cycle. Besides, the effect of subcooling, which means that the PCM solidifies at a temperature below the melting temperature, can in the worst case prevent the latent energy to be extracted from the system in the desired way [49]. In addition, a steady outlet temperature of the HTF is difficult to achieve with a latent storage compared to a sensible one, thus, cascaded storage arrangements are used [20]. Furthermore, the PCM experiences a volume dilatation around 10%, so that the capsules and/or the tank should be flexible enough to react on this volume change [49]. A stability over several cycles needs to be demonstrated in large scale. Kenisarin et al. [60] proposed 1000 cycles to prove the stability of the PCM. Besides, the corrosion of the tank due to the chemically aggressive PCM is also an issue that has to be considered [55]. The cycling behaviour is therefore estimated to be worse than the two tank molten salt reference system at the current status of research.

4.2.4. Maturity level

Latent energy storage concepts are still under development and have up to now only been tested on lab scale and not applied in large scale facilities [22].

4.2.5. Suitability for sodium

In general, latent storage systems are best-suited for direct steam generation. The charging and discharging of the storage and the steam production can be perfectly matched when the melting temperature of the PCM is close to the saturation temperature of the steam [53]. Therefore, in a sodium-based CSP plant only cascaded latent storages are suitable to match the temperature profile of the HTF (see Fig. 15). Furthermore, sodium has to be compatible with either the HX (finned tubes concept) or the

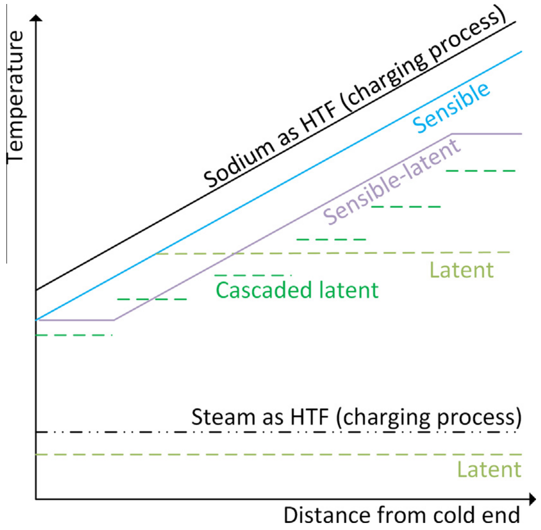

Fig. 15. Schematic profiles of the HTF and sensible and latent storage option during the charging process.

Table 6
Summary of evaluation of latent storage concepts.

Concept	Advantages	Disadvantages
Latent in general	+ Higher storage densities possible compared to sensible storage	– Higher cost possible compared to two tank system, but lack of data – Low maturity level – Large heat transfer surfaces required – Steady outlet temperature difficult to achieve
Finned tubes	+ Simplest latent system	– Thermal resistance in solid PCM during discharge – High cost HX
Packed bed PCM	+ Cost reduction, as no HX needed	– Complex flexible and sodium resistant capsules required, no known research done yet – Higher cost possible due to complex encapsulation
Screw type	+ Improved heat transfer due to constant removal of solid layer on heat transfer surface + Less heat transfer area necessary for a given storage capacity	– Moving system increases complexity and potentially cost

filler and tank material (packed bed concept). If there is a leakage, the sodium could pollute the PCM and vice versa. The possible reactions with the PCM (metals, chloride and fluoride salts) need to be investigated. However, the excellent heat transfer characteristics of sodium could be advantageous, as one of the main problems in latent systems is the tranfer of heat into and within the low thermal conductive PCM [1]. In a packed bed concept of encapsulated PCM, sodium could ensure a fast heat transfer to the capsules. However, the increasing heat transfer resistance in the growing solid layer during discharge within the PCM is still an issue. Thus, it is an important research issue to investigate in which extent the overall heat transfer can be actually improved.

A summary of the advantages and disadvantages of using latent storage systems in a sodium CSP plant can be found in Table 6. The evaluation of the latent heat storage concepts shows that all systems are on a lower maturity level, more complex, show a worse cycling behaviour and are possibly more expensive compared to the state-of-the-art system (two tank molten salt). However, concerning the storage density the latent storage concepts come off well. But it has to be noted that there is a lack of experimental data available in literature. The entropy generation could be further reduced by using a cascaded arrangement of the PCM which on the other hand leads to an increase of the complexity of the overall system. However, cascaded PCM systems are on an even lower maturity level than single PCM storages. The finned tubes concept is the least complex system, but the thermal resistance in the solid PCM at the wall reduces the heat transfer from the PCM to the HTF. In the screw type system, this is overcome as the solid layer is removed due to the actively moved PCM.

4.3. Combined sensible-latent storage systems

4.3.1. Storage medium cost

There is no data available for storage material costs for the proposed storage systems to the authors' knowledge, because this technology is still on a very early stage. As a conservative assumption, the costs are estimated to be in the same range as those of latent systems.

4.3.2. Storage density

One of the main advantages of the combined storage is the increased storage density compared to sensible heat storages [22,24]. The exact estimation of the storage density of a combined system depends on the specific materials.

4.3.3. Cycling behaviour

There is a lack of experimental data in the literature regarding the stability of combined systems over several cycles. Compared to the latent systems, a steady outlet temperature of the HTF can be achieved combining sensible filler material and a cascaded arrangement of the PCM capsules [26]. In the composite material the poor cycling behaviour of the PCM due to low thermal conductivities is improved by adding a highly conductive solid material (e.g. graphite) [25]. In conclusion, the cycling behaviour could be improved compared to sensible dual-media and latent systems.

4.3.4. Maturity level

The concept to combine sensible and latent heat storage is less developed than the sensible and the latent concept. Galione et al. [26] performed a numerical study of a multi-layered solid-PCM one tank system applied to a large scale CSP facility. On this basis Munoz-Sanchez et al. [22] proposed various PCMs, encapsulation and containment material for high temperatures. Furthermore, Zanganeh et al. [61] tested a high temperature combined thermocline on lab scale.

4.3.5. Suitability for sodium

Particulary the concept of a combined packed bed (Section 3.3.1) is promising for the use of sodium as HTF. The combination of sensible and latent storage material in a packed bed helps to overcome both the problems stated for sensible and for latent systems when using sodium as HTF. Firstly, by using PCM capsules in a packed bed additionally to solid filler material, thermal stratification can be enhanced [22,26]. This could be of particular interest for the use of sodium, as the PCM capsules layer form a temperature ”buffer” in a packed bed of solid material for sensible storage. Secondly, the addition of sensible filler material to a PCM capsules packed bed results in a better match of the HTF temperature profile (see Fig. 15). Similar to the latent system, sodium has to be compatible with the HX, filler and tank material. Hence, the same challenges have to be met as described for latent systems.

The advantages and disadvantages of the presented combined sensible and latent storage systems are summarized in Table 7. There is a lack of data available which complicates a differentiation of the concepts. The advantages of combined sensible and latent heat storage concepts are most of all the increased storage density compared to sensible storages and improved cycling behaviour. On the other hand these concepts are more complex, less mature and estimated to be more expensive than the reference molten salt two tank system. In the direct concept, on the one hand no HX is needed, which could lead to a cost reduction, but on the other hand resistant and flexible PCM capsules are needed, which could result in higher cost.

4.4. Thermochemical storage systems

4.4.1. Storage medium cost

As all the described thermochemical storage systems are still in an early stage of development, the costs are difficult to predict and therefore few data are available in the literature. The storage material costs of metal hydride are listed in Table 8 and vary from 5.3 to 17.4 $/kWh$_{th}$, which is in the same range as the listed sensible and

Table 7
Summary of evaluation of combined sensible and latent storage concepts.

Concept	Advantages	Disadvantages
Combined sensible and latent in general	+ Higher storage densities possible compared to sensible storage + Improved charging and discharging rates due to increased thermal conductivity	– Estimated higher cost compared to two tank system, but lack of data – Low maturity level – Increased complexity compared to sensible storage systems
One tank thermocline with PCM	+ Cost reduction, as no HX needed + Improved stability of the outlet temperature in a cascaded arrangement with filler	– Complex flexible and sodium resistant capsules required, no known research done yet – Higher cost possible due to complex encapsulation
Composite material (e.g. foams)	+ Direct contact of sodium with storage medium prevented	– High cost HX – Flexible foam required, that is compatible with volume dilatation during phase change
Gas as HTF with combined storage	+ Direct contact of sodium with storage medium prevented	– High cost HX

Table 8
Operating parameters and cost data of selected thermochemical storage materials: metal hydrides, ammonia and carbon hydroxide.

Medium	T_{reac} (°C)	p (MPa)	ρ (kg m^{-3})	$\Delta h_{reac,m}$ (kJ kg^{-1})	$\Delta h_{reac,V}$ (MJ m^{-3})	cost$_i$ ($ kg^{-1})	cost ($ kW^{-1} h^{-1})	Ref.
$NaMgH_3$	400–600	1–8	1000	1760	1760	4.2	8.6	[32]
NaH	400–600	0.05–7	750	2730	2047	4	5.3	[32]
$TiH_{1.72}$	650–950	0.05–1	1600	2485	3760	12	17.4	[32]
NH_3	700–800	20	n.a.	1964[*]	n.a.	n.a.	n.a.	[28,29,33]
$Ca(OH)_2$	507	0.1	n.a.	1343	1476	n.a.	n.a.	[28,34]

[*] Calculated with molar mass (NH_3) = 17,03 g/mol.

Table 9
Summary of evaluation of thermochemical storage concepts.

Concept	Advantages	Disadvantages
Thermochemical in general	+ Higher storage densities possible compared to sensible and latent storage + Products storable at ambient temperatures	– Lack of data on cost of storage system – Lowest maturity level – More cycling tests required
Metal/metal hydride – hydrogenation/ dehydrogenation	+ Simple product separation (solid/gas) + Good cycling behaviour	– Storage of hydrogen in high pressure vessels (or in a LTMH in a complex process) – High dissociation pressure at high temperatures
Ammonia/nitrogen/hydrogen – dissociation/synthesis	+ Low cost liquid educt at ambient temperature + Storage of products at ambient temperature	– High operating pressures – Storage of hydrogen and nitrogen in high pressure vessels – Incomplete conversion reaction
Calcium hydroxide/oxide – dehydration/ hydration	+ Low cost educts + Proven reversibility in 100 cycles + Low operating pressure (≈1 bar) + Easy product separation (solid/gas)	– Problems of agglomeration and sintering – Risk of sodium reaction in HX due to produced vater vapour in case of leakage

latent storage material costs. For ammonia and calcium hydroxide no values are given. However, Linder [28] stated that calcium hydroxide is available at low cost. However, the reactors including the HX and the storage of the reaction partners are the expensive components [28]. Luzzi et al. [62] assessed the costs of the ammonia inventory to be 1% of the overall storage costs. Therefore, the storage material itself can be assumed to be negligible compared to the costs for the remaining components of complex storage systems.

4.4.2. Storage density

Depending on the reaction enthalpy the storage density of thermochemical storage systems can be 15–20 times higher than latent or sensible storage systems [12,32]. In Table 8 the storage densities of the presented thermochemical storage materials are shown. They have a 3–6 times higher mass storage density and 2–4 times higher volumetric storage density compared to the reference molten salt storage (426.3 kJ/kg and 811,2 MJ/m^3).

4.4.3. Cycling behaviour

In case of the hydroxide reaction, reversibility over more than 100 cycles has been shown, but in case of the ammonia dissociation incomplete conversion of the reactions was reported by Pardo et al. [29]. The heat transfer to the reaction partners has to be ensured by a large heat transfer surface or a moving system.

4.4.4. Maturity level

The tests of the thermochemical systems are still on lab to pilot scale and are less developed than latent concepts [12].

4.4.5. Suitability for sodium

Thermochemical storage systems are still on an early stage of maturity, therefore, system issues still need to be further investigated and the advantages or disadvantages when using sodium as HTF are difficult to estimate. However, the excellent heat transfer characteristics of sodium could possibly provide an improved heat transfer to the thermochemical storage material. Furthermore, all thermochemical systems are indirect systems. Thus, if there is a leakage in the HX, sodium could mix with the storage medium. It needs to be investigated which reactions could occur. For example water, with which sodium reacts strongly exothermically, is one of the products of the hydroxide reaction.

In Table 9, the main advantages and disadvantages of the thermochemical storage systems proposed in this section are summarized. Thermochemical storage systems stand out due to their 15–20 times higher storage density compared to sensible or latent systems. But compared to the reference system a sufficient cycling behaviour still needs to be demonstrated and the maturity level is lower. Besides, the complexity of the system and hence the costs are estimated to be higher at the current state of research. The ammonia dissociation and the hydroxide reaction are those thermochemical storage systems with the highest potential due to long term experience.

5. Conclusion

In this paper, sensible, latent, combined sensible-latent and thermochemical storage systems have been presented and evaluated systematically on the basis of selected criteria. It is stated that the maturity level of the presented storages generally decreases in the listed order. However, the interest in these systems recently increases in this order due to increasing storage densities. For molten salt CSP plants the state-of-the-art storage system is the two tank molten salt storage. For sodium, however, other storage options are more advantageous. The systems that are of particular interest are listed below.

- Sensible: one tank sodium thermocline.
- Combined sensible-latent: one tank thermocline with filler and PCM capsules.
- Thermochemical: ammonia dissociation/synthesis.
- Thermochemical: calcium hydroxide/calcium oxide.

The direct one tank system with filler material (see Section 3.1.2) is a very promising system as no HX is needed. Furthermore, this system has already been investigated for molten salt and thermal oil [38,41]. Compared to the direct two tank system the amount of sodium can be significantly reduced. At the same time this leads to an increase of volumetric density of the storage, therefore smaller tanks are needed for a given storage capacity. However, the cycling behaviour, in particular if a thermal stratification with the highly thermal conductive sodium can be achieved, and the chemical compatibility with the filler material need to be investigated.

The one tank system with filler material and PCM capsules (Section 3.3.1) combines the advantages of a sensible storage system (high thermal conductivities, temperature profile of HTF matched) and the advantages of a latent storage system (increased storage density, temperature ”buffer”). However, it is a more complex and less developed system than the sensible one tank system and the cycling behaviour and chemical compatibility with the PCM capsules are proposed to be a subject of research.

The thermochemical storages with ammonia or calcium hydroxide (Sections 3.4.2 and 3.4.3) are highly interesting due to their large storage densities. Additionally, these reactions have been intensively investigated both theoretically and experimentally in the past. However, a complete reversibility still needs to be shown for the ammonia dissociation and besides, high operating pressures up to 30 MPa [33] are needed for the reaction and the storage of the products. Calcium hydroxide, in contrast, reacts at ambient pressure and the reversibility has been shown in 100 cycles, but problems of agglomeration and sintering occured [28]. Due to its excellent heat transfer characteritics, sodium could provide a good heat transfer to the reactants. To which extent this could be an improvement for thermochemical storage, has to be shown in the future.

As the thermochemical storage systems are still on a very low maturity level, a sensible one tank thermocline system with filler material, upgradeable to a one tank system with sensible and PCM filler to increase the storage density and improve the thermal stratification, is proposed as the most promising TES system in a sodium CSP plant at the current state of research. Further research should be done in the field of thermochemical systems to bring more reliability into their applicability in a sodium-cooled central tower system.

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