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Molten Salt Storage for Power Generation

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Storage of electrical energy is a key technology for a future climate-neutral energy supply with volatile photovoltaic and wind generation. Besides the well-known technologies of pumped hydro, power-to-gas-to-power and batteries, the contribution of thermal energy storage is rather unknown. At the end of 2019 the worldwide power generation capacity from molten salt storage in concentrating solar power (CSP) plants was 21 $\mathrm{GWh_{el}}$. This article gives an overview of molten salt storage in CSP and new potential fields for decarbonization such as industrial processes, conventional power plants and electrical energy storage.

Keywords: Combined heat and power, Concentrating solar power, Power-to-heat, Thermal energy storage, Waste heat recovery

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1 Commercial Molten Salt Storage Systems in Concentrating Solar Power Plants

Concentrating solar power (CSP), also known as solar thermal electricity, is a commercial technology that produces heat by concentrating solar irradiation. This high-temperature heat is typically stored and subsequently used to generate electricity via a steam turbine (Rankine cycle) [1]. In other words, the thermal energy storage (TES) system corrects the mismatch between the unsteady solar supply and the electricity demand. The different high-temperature TES options include solid media (e.g., regenerator storage), pressurized water (or Ruths storage), molten salt, latent heat, and thermo-chemical [2]. At the time of writing, commercial CSP systems utilize almost exclusively sensible heat storage with molten salts (Figs. 1 and 2). Similar to residential unpressurized hot water storage tanks, high-temperature heat (170–560 °C) can be stored in molten salts by means of a temperature change. For a given temperature difference $\Delta T = T_{\mathrm{high}} - T_{\mathrm{low}}$, the heat (or inner energy) Q_{Sensible}, which can be stored is given by Eq. (1) as follows:

$$Q_{\mathrm{sensible}} = m \cdot c_{\mathrm{p}} \cdot \left(T_{\mathrm{high}} - T_{\mathrm{low}}\right) = m \cdot c_{\mathrm{p}} \cdot \Delta T \tag{1}$$

Hereby, c_{p} is the specific heat capacity of the molten salt, T_{high} denotes the maximum salt temperature during charging (heat absorption) and T_{low} the temperature after discharging (heat release).

The following three subsections describe the state-of-the-art technology and current research of the molten salt technology on a material, component and CSP system level.

1.1 Molten Salt as Heat Transfer and Storage Medium

Molten salts used for TES applications are in solid state at room temperature and liquid state at the higher operation temperatures. High-temperature properties such as the volumetric storage density, viscosity and transparency are similar to water at room temperature. The major advantages of molten salts are low costs, non-toxicity, non-flammability, high thermal stabilities and low vapor pressures. The low vapor pressure results in storage designs without pressurized tanks (Fig. 1). Molten salts are suitable both as heat storage medium and heat transfer fluid (HTF). In general, there is experience with molten salts in a number of industrial applications related to heat treatment, electrochemical treatment and heat transfer for decades.

For molten salt, the lower and upper temperature thresholds must be taken into account. The upper limit can be determined by the thermal stability, the metallic corrosion rate and other thermo-physical limitations (e.g., high vapor pressure). Salts are typical classified by the anions which mainly determine the chemical properties (e.g., nitrates, nitrites, chlorides, carbonates). The lower limit is defined by the melting temperature, which can vary significantly

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Figure 1. Example of a 1000 MWh_{th} two-tank molten salt storage system of a concentrating solar power plant in Spain (Source: Andasol 3).

depending on the anion type and the cation composition. Mixtures of different salts have the advantage of lower melting temperatures, compared to their single salts, but can exhibit similar thermal stability limits. Hence, salt mixtures can have a larger temperature operation range and a lower risk of freezing compared to single salts.

For energy storage in CSP plants, mixtures of alkali nitrate salts are the preferred candidate fluids. These nitrate salts are widely available on the fertilizer market. Liquid thermophysical properties of typical mixtures are available in literature [3, 4]. In commercial CSP plants, almost exclusively a non-eutectic salt mixture of 60 wt % sodium nitrate and 40 wt % potassium nitrate is utilized. This mixture is commonly referred to as *Solar Salt*. Solar Salt is an optimized mixture with regard to melting temperature, single salt costs and heat capacity. The minimum operation temperature of Solar Salt is typically set to 290 °C (limited by the liquidus temperature of about 250 °C plus a safety margin). The maximum operation temperature is about 560 °C, mainly defined by thermal stability. For a temperature difference of 250 K, the volumetric heat capacity, i.e., “storage density” of the medium reaches a value of about 200 kWh m^{-3}. The molten salt medium related costs make up typically a significant proportion of the overall TES system costs. For large-scale systems, molten salt costs are currently in a range from 4–20 € kWh_{th}^{-1} depending on exact market prices and temperature difference.

The material research on molten salt related aspects is diverse. Some review and overview publications on molten salt and other storage materials are available [2, 5–10]. Tab. 1 summarizes major molten salt material research topics in the CSP field.

1.2 Molten Salt Thermal Energy Storage Systems and Related Components

State-of-the-art molten salt based TES systems consists of a “cold” (e.g., 290 °C) and a “hot” (e.g., 400 °C or 560 °C) unpressurized flat bottom tank. Each tank has a foundation, insulation, pumps and instrumentation (temperature, pressure, salt level, flow). At the time of writing, the maximum fluid height is about 13 m and the maximum diameter is about 40 m, which allows for the storage of roughly 30 000 t of molten salt in a single tank. The temperature in each tank is kept constant. The fluid level of the tanks changes during charging and discharging. A small amount of molten salt always remains at the bottom of each tank (tank sump). Currently there are commercial CSP plants with molten salt storage units up to about 4000 MWh_{th} (Solana in the US). Such large-sized storage units use several pairs of hot and cold tanks.

Unlike other TES technologies (e.g., solid media regenerator or pressurized water type TES), two-tank molten salt storage systems provide constant power and temperature levels throughout the entire charge and discharge process, whereas other technologies typically show a drop of the temperature, power or pressure level during discharging. This drop can have a negative effect on the performance of subsequent system (e.g., a power block). For molten salt storage, the components for capacity (tanks) and power (e.g., heat exchanger) are fully separated (Fig. 2) and this configuration allows for constant power and temperature levels. The size of exchanger is only determined by the necessary power and not by the capacity of the storage unit. This is a significant advantage of the two-tank molten salt storage system, which simplifies its operation and also design adaption. For example, enhancing the storage capacity requires no extra investments for power components (e.g., electrical heaters, heat exchangers) but only larger tank units filled with salt. Hence, for a given thermal power, the increase in investment costs for additional storage capacity is relatively small. This stands in contrast to batteries, where capital costs scale linearly with capacity.

The research on molten salt storage on component level is manifold and summarized in the following Tab. 2. The component research is not limited to the molten salt tank systems but also focuses on power components and other components in the molten salt loop (e.g., pumps, valves, instrumentation), as well as fundamental process technology aspects (e.g., salt freezing).

In order to examine component related aspects, typically molten salt test facilities are utilized. The DLR owns a facility which allows experimental work on single tank concepts (TESIS:store facility, Fig. 3) and qualification of components in a test section (TESIS:com facility). Details of this plant can be found in literature [33, 34].

1.3 Integration of Molten Salt Storage in CSP Plants

The commercial status of high-temperature TES makes CSP a unique application. By storing the thermal energy, CSP is able to firmly deliver electricity on demand. This ability to provide electricity on demand makes CSP stand out from

Table 1. Molten salt research topics on a material level in the CSP field.

Objective, motivation and technological challenge	Material research topics
Related to *new parabolic trough systems* with molten salt as HTF (currently thermal oil is commercially utilized), there is a need to identify salt mixtures with a lower operation temperature. Main reasons are lowering the risk of salt freezing and thermal losses at night in the large parabolic trough solar field. To some extend lowering of salt mixture costs with calcium nitrate is anticipated.	The interest is the identification of (*multi-component*) *mixtures with lower melting temperature* by phase diagram measurements and computational determination of phase diagrams. Mixtures are also optimized in terms of costs, melting temperature, stability, density, and heat capacity. The work is mainly related to nitrate-nitrite mixtures [3, 9, 11–15], but also some work for chlorides exists [16, 17].
Mainly related to the *CSP power tower* systems molten salts with higher operation temperature would be favorable. This could result in a higher reliability (e.g., temporal and local overheating could be accepted; larger safety margin), larger temperature differences power components leading to lower power components costs (e.g., solar receiver, electrical heater, steam generator) and higher Carnot efficiencies of power cycles (e.g., new cycles with CO_2, higher steam parameters for Rankine cycle)	The interest is optimization and identification of *molten salts mixtures with higher operation temperature*. One research line is the optimized operation of existing Solar Salt [18, 19]. Other work focuses on the identification and qualification of new salt classes. Of major interest are carbonate [20, 21] and chloride salt mixtures. At the time of writing chlorides rather than carbonates seem to be the preferred option (mainly due to higher costs for carbonates) [22–24]. One major challenge of chlorides is the corrosively with metallic aluminizing/coating, salt additives, salt purification approaches to overcome this aspect [25, 26].
Higher impurity levels in molten salt are a major concern since they can accelerate *metallic corrosion*. Molten salt impurities can originate from the atmosphere (e.g., carbonates from CO_2, hydroxides from moisture), delivered grade of salt (e.g., chlorides), salt hydrolysis (e.g., hydroxide species), salt thermal decomposition (e.g., oxides) and structural metals (e.g., formation of chromates).	Molten salt corrosion research is diverse with several aspects affecting the corrosion rate. They include salt composition, salt impurities, atmospheric conditions, type of structural metal, treatment of metals (e.g., surface finishing, heat treatment) and application related aspects (e.g., additional mechanical loads, temperature changes and gradients, welds and welding additives, salt flow, salt-gas boundary layers). For CSP, metallic corrosion research focuses on carbon and stainless steels, as well as nickel based structural alloys for nitrates, chlorides and carbonates. For sealing some other metals are also of interest [26–32].
Molten salt loops typically consist of several components (e.g., pumps, valves, flanges, instrumentation) with a requirement to utilize not only structural metals but also other *additional non-metal materials with molten salt compatibility requirements*. Also there is interest to replace molten salt by an inexpensive filler material to reduce capital costs.	The compatibility of non-metallic materials in contact with molten salt for moving parts (e.g., in valves and pumps), removable connections (e.g., seals for flanges) and electrically insulating parts (e.g., instrumentation) are of interest. Examples of examined materials include graphite, ceramics, and glass [5]. Natural rocks and waste product from the process industry were also examined in direct contact as inexpensive filler materials [33–35].
From a scientific point of view with some relation to the molten salt technology, a better *fundamental understanding of molten salt mixtures* is of interest.	Some examples of fundamental work on molten salt mixtures include the following list: molecular dynamic modeling and prediction of mixture behavior [36]; improved thermophysical properties with nano-additives, [37]; calculation /correlation of temperature dependent physicochemical properties from single salt components [38, 39]. In general there is also some knowledge available from other molten salt applications than CSP (e.g., nuclear industry, metal processing) which can be adapted or is applicable to CSP.

other volatile renewable energy technologies like photovoltaics and wind. Further advantages of TES integration include the following:

- If a backup ability for the plant is necessary, only the additional cost for the installation of a gas heater is necessary. Hence, backup and plant availability can be ensured at low cost (e.g., compared to other solutions like batteries which would require a complete power plant as backup).
- Although additional investment costs due to TES are added, 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 (avoiding strong gradients for connected components, e.g., piping, heat exchanger, boiler, turbines) which increases the lifetime of components.
- The size (or capital cost) of subsequent components, e.g., evaporator, condenser, boiler, turbines, can be reduced.
- TES allows improved thermal management of the solar system (e.g., faster start-up time, accurate preheating of solar steam cycle, avoid surplus energy, cover peak demand).

By the end of 2019 the worldwide dispatchable power generation from molten salt storage in CSP plants was about 3 GW_{el} with an electrical storage capacity of 21 $GWh_{el.}$ This results in an average storage duration of

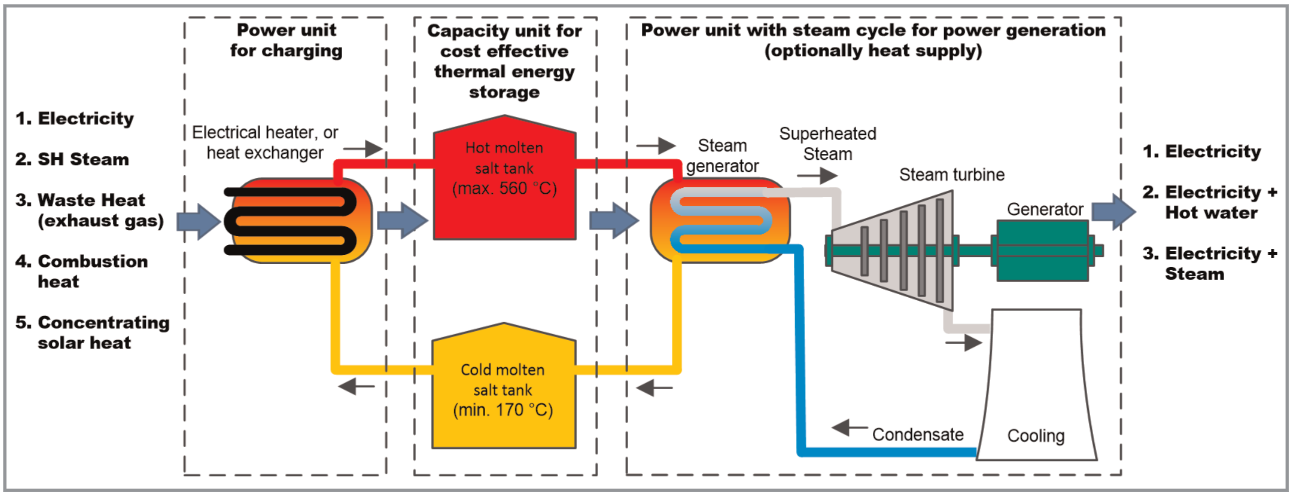

Figure 2. Options for the utilization of molten salt storage technology with three subsystems: power unit for charging (left); capacity unit for storage (middle); power generation unit for discharging (right) (Source: DLR).

Table 2. Molten salt research topics on a component level in the CSP field.

Objective, motivation and technological challenge	Component research topics
Objectives for the *molten salt tank system* are improvements of the reliability and overhauling concepts, higher operation temperatures, as well as the reduction of operational expenditure (OPEX) and capital expenditure (CAPEX). Cost saving are feasible with single tank concepts compared to two tank concepts. Single tanks remain filled during operation with characteristic temperature zones (hot salt at the top, cold salt at the bottom and thermocline zone in between).	Research on *two tank* optimization addresses aspects such as foundation design, heat losses, temperature distribution within the tanks and startup procedures [40–45]. Recently a best practice study including tank aspects was also published [46]. The major motivation for *single tank* storage concepts are cost savings. The major research line is currently single thermocline tanks with inexpensive filler materials [47–52], but also some work on the single tank moving barrier concept [53] and natural stratification [48], both without filler exist.
Furthermore, improvements of power components in the molten salt loop to add or remove heat are addressed. For heat charging solar receivers/absorber, combustion heaters, electrical heaters, and heat exchangers are of interest. Heat discharging requires mainly heat exchangers and steam generators.	Recently a best practice study including power component aspects was published [46]. Examples of related research work are listed below: – Solar receiver/absorbers for trough [54] and towers [55] – Electrical heater [56] – Combustion heater (melting units are commonly used) – Heat exchangers for flue gas from a gas turbine peak power plant [57] – Heat exchangers for thermal oil [58] – Steam generators [59–63]
Besides power and storage components, there are some *additional molten salt components, as well as fundamental and process technology* related aspects of technological importance. Objectives are for example enhanced reliabilities, higher operation temperatures and higher measurement accuracies, as well as reduced OPEX and CAPEX. In general there is also experience from nuclear molten applications and some review literature refers to the nuclear field.	Additional components in molten salt loops [40, 64] include pumps [65], valves [66–68], flanges and seals [5], flexible hoses [69], melting units [70], auxiliary heating, piping and support, insulation [71], as well as measurement equipment for temperature, pressure, flow, and level [72, 73]. One aspect with molten salts is unwanted freezing during operation. Freezing must be prevented in the piping, the heat exchanger and in the storage tanks. Re-melting after freezing and possible damage was also examined [72]. A review of fundamental work on forced convection molten salt heat transfer is also available [74].

about 7 h (21 GWh/3 GW) with a total range from 3 h to 15 h. The total thermal capacity is 50 to 60 $\mathrm{GWh_{th}}$ (estimated from 21 $\mathrm{GWh_{el}}$ and typical conversion efficiencies) [1]. At the time of writing, typical capital costs of large-scale molten salt storage systems range from 15 to € 80 $\mathrm{kWh_{th}}^{-1}$ depending on parameters such as scope of delivery, capacity and power level as well as the temperature difference between hot and cold tank. It is important to note that the specific storage costs (in € $\mathrm{kWh_{th}}^{-1}$) can be reduced considerably, when the storage system is implemented in systems

Figure 3. DLR Test Facility for Thermal Energy Storage in Molten Salts (TESIS) in Köln, Germany.

with larger temperature differences. That is due to the direct proportionality between the capacity of a molten salt storage and the temperature difference between the hot and the cold tank (see Eq. (1)).

In general, there are two commercially realized molten salt storage configurations. They are called direct and indirect configuration. Indirect storage refers to systems with a different HTF and storage medium (Fig. 4a), whereas direct storage systems (Fig. 4b) utilize a single medium as HTF and storage medium.

The availability of experiences from the CSP project Solar Two in the US was a major benefit for the molten salt development and commercial implementation. Based on the Solar Two experience, molten salt was selected for the Andasol power plants in Spain using parabolic trough technology (Kelly 2006). The Andasol power plants are the first large-scale examples of the indirect storage systems (Fig. 4a) with a capacity of about 1000 MWh_{th} and a storage duration of about 7.5 h [70]. The cold tank temperature was set to 292 °C with a safety margin to the liquidus of Solar Salt. The hot tank temperature was set to 386 °C due to the upper temperature limit of the thermal oil (max. 393 °C), used as primary heat transfer fluid in the solar field. The difference between oil temperature and salt temperature is due to the temperature difference in the molten salt-thermal oil heat exchanger. Subsequently, a few dozen plants, often in a similar configuration were installed around the world. A detailed list of installed plants can be found elsewhere [75].

The first demonstration of a direct storage concept is the Solar Two central receiver power plant using molten salt both as HTF and heat storage medium. This demonstrational power plant was erected in 1994 on basis of the Solar One facility and was operated until 1999. The maximum electrical power was 11 MW_{el}. The two tank storage system with a total volume of about 1700 m^3 had an inventory of 1400 t of Solar Salt. Operation temperature was between 290 °C and 565 °C and virtually all subsequent tower plants used similar temperature levels. The thermal capacity of the storage system was 107 MWh_{th}, which allowed the

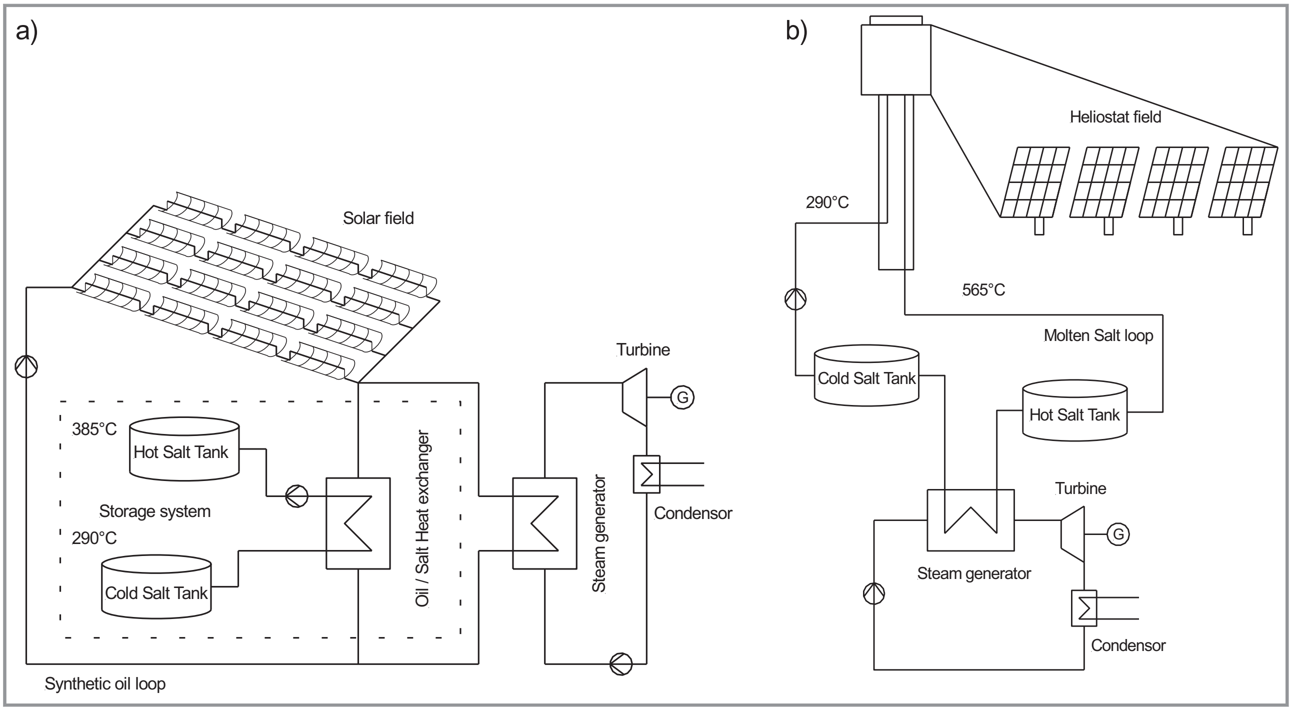

Figure 4. Simplified scheme of a parabolic trough power plant with an indirect molten salt storage system (a) and solar tower plant with central receiver with a direct storage molten salt storage system (b).

operation of the turbine for 3 h [76]. The first commercial solar tower power with direct two-tank storage system was the Gemasolar plant in Andalusia, Spain, which went in operation in 2011 [77]. The Gemasolar plant has an electrical power of 20 MW_{el}, storage temperatures of 292 and 565 °C and a storage capacity of 15 h. This storage size allows 24 h operation. Subsequently, larger tower plants with direct storage went in operation or are under construction [75, 78, 79]:

- Crescent Dunes 110 MW_{el}, US
- NOOR3 134 MW_{el}, Morocco
- DEWA CSP Tower 100 MW_{el}, United Arab Emirates
- Atacama-1 110 MW_{el}, Chile
- Golmud 200 MW_{el}; Hami CSP Project 50 MW_{el}; Luneng Haixi 50 MW_{el}; Qinghai Gonghe 50 MW_{el}; Shouhang Dunhuang 100 MW_{el}; SUPCON Delingha 50 MW_{el} and Yumen 100 MW_{el}, all China.

Hence, at the time of writing, central receiver power plants with molten salt both as HTF and heat storage medium are the commercial standard for large-scale tower systems. The research on overall CSP system integration and optimization of molten salt storage is related to different topics as shown in Tab. 3.

It can be summarized that molten salt research addresses the entire value chain with material, components and system related aspects. The following text discusses new opportunities for molten salt storage systems. Unlike CSP, no commercial examples are known for these new potential fields of application at the time of writing.

2 Molten Salt Storage Opportunities for Energy-Intensive Industrial Processes

One application is the improvement of the energy efficiency within 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. Processes and applications for TES are diverse. Examples are waste heat recovery in flue gas, improved heat integration of batch processes, backup heat, buffering of fluctuating waste heat streams and

Table 3. Molten salt storage research topics on CSP system level.

Objective, motivation and technological challenge	Research topics on CSP system level
Molten salt storage sets the commercial standard in CSP plants at the time of writing. Major indicators to evaluate and compare storage systems are the capital cost of the TES system and the LCOE. Several *other TES technologies* are developed for CSP. Cost figures are compared to some extent with the two tank molten salt configuration as a reference.	*Comparison of two-tank molten salt storage* system in CSP with *alternative technologies* using other storage materials and HTFs [2, 10, 80–84]: – sensible heat storage in liquids, e.g., pressurized water [79], thermal oil [85], molten metal [86], – sensible heat storage in solids, e.g., structured or packed bed ceramics [87], concrete [88], moving particles [89] – latent heat with phase change materials [90] – thermochemical, e.g., calcium oxide/calcium hydroxide conversion [91, 92].
Molten salt power tower and parabolic trough with thermal oil and molten salt TES is established commercial standard configuration at the time of writing. The decrease of LCOE is a major motivation for research on *novel CSP configurations with molten salt storage.*	Theoretical and experimental assessment of CSP configuration with molten salt storage. This includes established configurations, e.g. molten salt power tower [40, 76] and parabolic trough with thermal oil [41, 93], as well as *novel CSP configurations*, e.g. direct parabolic trough with molten salt [94, 95], linear Fresnel [96], supercritical steam [97–99], supercritical CO_2 cycles [22, 98, 100], higher operation temperatures with carbonate or chloride salt [22, 97], solar gas turbines with Rankine bottom cycle [98], power tower topping cycle with molten metal [97, 86], hybrid CSP-fossil-plants, e.g. with natural gas or coal [83, 98, 101–103], hybrid CSP plants with integration of photovoltaics (e.g., PV/CSP hybrid plant in Morocco, [98, 104, 105].
CSP system modeling and simulation with a molten salt two tank storage system can be considered as straightforward. The two tank system has separate components for power (e.g., heat exchangers, pumps) and capacity (storage tanks). Hence, the power and temperature level for charge and discharge are constant (except startup and shutdown procedures). For the molten salt *single tank* technology, system simulation is more challenging due to a change of the exit temperature at the end of the charging and discharging process, as well as self-discharge of the single tank. This requires transient modelling with the ability to accurately model part-load behavior.	Thermodynamic inefficiencies caused by the *thermocline* can be assessed by overall CSP plant simulation using LCOE as evaluation criterion. The performance of single tank thermocline was compared to two-tank systems by different authors [106–108].

stabilizing of steam supply as well as improved electrical load management with power-to-heat (PtH) and TES. Typically the potential of high-temperature molten salt storage is not within the process but at the process interfaces as shown in Fig. 5.

There is a major need to identify flexibility options of energy-intensive processes for the integration of volatile renewable electricity and decarbonization of energy-intensive processes. Flexibility options were addressed by the Kopernikus Project SynErgie in Germany [109]. Selected large-scale processes in the energy-intensive process industry were examined. It was shown that some glass furnaces already operate in hybrid mode with gas firing and electricity to supply heat. The ability to switch between gas and electricity results in a flexibility option for the electrical grid.

Fig. 5 on the top shows a novel potential concept for hybrid operation with a molten salt storage system. Processes which already (e.g., salt reactors in the chemical industry) or potentially utilize molten salt as HTF could operate flexible on fuel or electricity. This concept can provide a large flexibility option to the grid. It may be feasible to utilize renewable electricity peaks to a larger extent (e.g., midday photovoltaic peak) due to affordable costs of photovoltaics and PtH for molten salt systems.

Fig. 5 on the bottom shows schematically the molten salt storage integration using output heat streams (e.g., hot products, flue gas). There is a potential for TES if the output heat stream is unsteady (batch process) or the subsequent process requires heat with a temporary shift. For molten salt storage the electric arc furnace for steel melting as a batch process was examined. Potentially intermittent waste heat in the flue gas stream could be recovered. Required components are a molten salt flue gas heat exchanger, molten salt storage system, molten salt steam generator and a steam turbine. For example, a steam turbine could continuously generate about 5 $\mathrm{MW_{el}}$ for a typical electric arc furnace with 100 $\mathrm{MW_{el}}$ input power [110]. Such a steam turbine could generate electricity only or combined heat and power (CHP).

3 Molten Salt Storage Opportunities for Conventional Power Plants

Photovoltaics and wind increasingly displace conventional generation. This leads to an increasingly variable operation of conventional power plants with load following, reduced capacity factors and increased number of startups accompanied by thermally stressed components and reduced lifetime [111]. To diminish these drawbacks, molten salt storage can be integrated in conventional power plants. Applications and benefits of power plant concepts with an integrated high-temperature molten salt storage are summarized in the following Tab. 4. TES can also provide the services listed above for electrical grid storage, which is discussed in the following section.

4 Molten Salt Storage Opportunities for Electrical Storage

Bulk grid-connected electrical storage is dominated by pumped hydroelectric energy storage (without TES) [1]. 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 electricity sources. Currently, several electrical storage concepts including a large-scale TES system are examined [119–121]. These non-commercial electrical storage concepts with a relation to molten salt storage are listed in the following Tab. 5.

Besides PtHtP, power-to-gas-to-power (PtGtP) is a major concept for large-scale energy storage. The following Fig. 6 compares the PtHtP with PtGtP concept. On the right-hand side the energy Sankey diagram of the PtGtP is shown. The PtGtP conversion efficiencies are taken from available published data [131]. It can be seen that the efficiency from electricity-to-electricity of PtGtP is only about 25 %, if the entire conversion chain is considered. This is due to larger losses for the electrolysis, methanisation and compression processes. The combined heat and power potential can be considered to be limited, because the dispatchable heat for

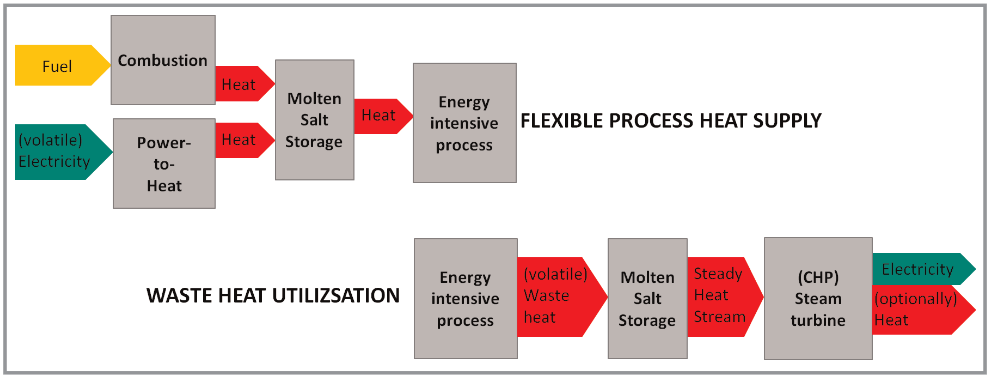

Figure 5. Potential utilization options of molten salt storage technology in energy-intensive industrial processes: flexible process heat supply (top) and waste heat utilization (bottom) (Source: DLR).

Table 4. Molten salt storage research topics for conventional power plants.

Objective, motivation and technological challenge	Research topics on system level for conventional power plants
For conventional power plants TES integration can contribute to a higher *flexibility* of electricity generation and thermal management (e.g., faster gradients, reduction of minimum load and improved part load, component preheating, improved availability, backup heat). This higher flexibility would allow for additional volatile wind and PV installations while ensuring security of electricity supply with flexible conventional power plants.	Drost proposed a coal fired peaking power plant using molten salt storage in 1990 [112]. Conventional power plant operation with a higher flexibility using TES was examined in research projects (e.g., BMWi funded projects FleGs 0327882 and FLEXI-TES 03ET7055). Garbrecht simulated molten-salt thermal storage systems in an incinerator and a small-size lignite-fired power plant [113]. Wojcik reviewed literature about TES in power plants and examined TES concepts in the steam-water cycle at different integration points [114].
Direct integration of volatile wind and PV electricity in conventional power plants is examined. These *hybrid* configurations with two energy inputs allow a "fuel switch". An example is the combination of fuel combustion and volatile wind and photovoltaic electricity via power-to-heat (PtH) and TES. The molten salt storage transforms the volatile electricity into a steady heat flow for the power cycle.	Several studies on hybrid configurations of volatile wind and PV electricity with other sources have been published. Examples include the combination with nuclear power [115], coal power (e.g., German project Store-to-Power), the combination of natural gas combustion with molten salt storage integration in combined cycle plants [111, 116].
Conventional *combined heat and power* (CHP) units operate typically 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. Also hybrid supply of CHP via high-temperature heat storage is feasible.	The authors proposed to operate steam turbine CHP plants supplied by a molten salt storage in hybrid charge mode with fuel combustion and volatile electricity via PtH technology. Heat could be supplied to district heating or as process steam [117, 118].

end-use is considered to be only about 13 % (about half of the value of the electrical output) [131].

On the left-hand side of Fig. 6 the energy Sankey diagram of the PtHtP is shown. The PtHtP storage solution is considered to be more efficient compared to the PtGtP solution. For the given example, it can be expected that the electrical round-trip efficiency is about 19 %. This electrical efficiency is mainly limited by the conversion efficiency of the steam turbine. Unlike for the PtGtP storage option, a large share of up to 68 % could be available as dispatchable heat (e.g., steam) for further end-use. Hence, PtHtP is suitable for CHP operation and it could have high overall efficiencies of 80–90 % (Fig. 5).

Tab. 6 summarizes the pros and cons of the PtHtP and the PtGtP storage options. PtHtP is advantageous in terms of electrical efficiency and CHP efficiency compared to PtGtP. Also investment costs for power components of PtHtP could be lower (e.g., electrical heater for charging) compared to PtGtP (e.g., electrolysis, methanisation). On the other hand, PtGtP allows for inexpensive bulk storage and transport of gas over long periods (weeks), whereas TES of PtHtP is typically cost effective for daily charging. Hence, a hybrid storage solution is proposed which combines the advantages of the PtHtP and PtGtP technologies (Tab. 6). Fig. 6 in the middle shows an example with an arbitrarily chosen ratio of 75 % PtH and 25 % power-to-gas supply. This ratio can be adjusted and optimized depending on the needs for electrical efficiency, share of process heat, investment costs and demand of short and long duration storage. One main reason for the hybrid storage solution (rather than two individual storage systems) could be the reintegration of some of the flue gas heat of the gas turbine into the PtHtP process in order to increase the conversion efficiency. The heat reintegration could also reduce the payback period of the molten salt storage and the steam turbine system due to twofold use cases with two TES charging options (electricity and gas turbine flue gas). The PtHtP and gas turbine could be situated in one site as a "storage plant" (see also [116]). For CHP operation, the storage plant could be located close to the end-use as an "on-site storage plant". The remaining PtG unit could be installed at another location close to the supply of volatile electricity for example close to an offshore wind site.

5 Summary and Conclusion

The article gives an overview of molten salt thermal energy storage (TES) at commercial and research level for different applications. Large-scale molten salt storage is a commercial technology in the concentrating solar power (CSP) application. The worldwide installed capacity is 21 $\mathrm{GWh_{el}}$ or about 60 $\mathrm{GWh_{th}}$ with an average storage duration of 7 h. The major advantages of molten salt thermal energy storage include the medium itself (inexpensive, non-toxic, non-pressurized, non-flammable), the possibility to provide superheated steam up to 550 °C for power generation and large-scale commercially demonstrated storage systems (up to about 4000 $\mathrm{MWh_{th}}$) as well as separated power components (e.g., heat exchangers) and capacity components (tanks) for constant temperature and power levels during charge and discharge.

Decarbonization of the diverse energy intensive industrial processes remains a major challenge. The potential for the

Table 5. Molten salt storage research topics for bulk electrical storage systems.

Objective, motivation and technological challenge	Research topics on system level for bulk electrical storage systems
Power-to-heat-to-power (PtHtP), also called electrothermal energy storage (ETES), utilize a PtH component for charging, a TES and different devices for discharging. For the power cycles, such as Rankine and Brayton, the efficiency is limited by the Carnot efficiency. Although turbomachines limit the efficiency during discharge, the PtH component for charging can be relatively inexpensive and hence PtH provides an efficient way to absorb short and large peak power (e.g., photovoltaics during midday). Further advantages include high life expectancies in the range of 20–30 years, low capacity-specific costs (€ kWh^{-1}), a low environmental impact and flexibility regarding the sites.	At the time of writing, the conversion of conventional coal power plants in Germany into PtHtP is considered. One major motivation is the reuse of existing infrastructure (e.g., steam turbine, generator, cooling tower, grid-connection) and staff on-site. In the research project StoreToPower the potential of the full conversion of lignite coal power plants in the Rhineland area to PtHtP-Storage systems with large sized molten salt storage systems is theoretically examined [122]. Kosman compared different options of molten salt storage integration for the transition from coal to green energy power systems [123]. At the time of writing, there are also different industrial initiatives for PtHtP with molten salt (e.g., MOSAS from MAN, eTES from Flagsol, Pintailpower).
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 power cycle. There are several types of cycles (e.g., Brayton, Rankine), working fluids (e.g., air, CO_2, 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 of interest. The advantages of PTES are similar to the PtHtP concept: high life expectancies, low capacity-specific costs, low environmental impact and site flexibility. Utilization of a heat pump makes PTES a concept with a higher maximum efficiency (100 % if considered isentropic) at the expense of a more complex system compared to PtHtP.	Aga proposed the use of CO_2 cycle PTES to store volatile photovoltaic electricity via cold water and hot molten salt storage [124]. Laughlin proposed a PTES concept based on closed-cycle Brayton cycle with cold hexane and hot molten solar salt storage [120]. Vinnemeier et al. provided a characteristic diagram which allows to identify the most reasonable heat pump working fluid and process configuration referring to the boundaries of a specific storage concept [125]. McTigue investigated different PTES concepts with supercritical CO2 cycles with molten salt storage with and without concentrating solar heat input [126]. Steinmann compared five different PTES concepts including molten salt storage [127].
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 could store compression heat during charging and preheats air during discharging in order to increase the round trip efficiency. Different TES options such as solid media and molten salt are feasible. This concept has also a theoretical efficiency of 100 % when considered to be isentropic and is called Adiabatic Compressed Air Energy Storage (A-CAES).	The ADELE-ING Project examined solid media regenerator, molten salt and thermal oil as TES options for A-CAES [128]. Grazzini performed a thermodynamic analysis of the design parameters and influence on system efficiency of multistage Adiabatic CAES [129]. Chen reviewed work on CAES, A-CAES and discussed also utilization of molten salt storage [130].

Table 6. Simplified comparison of PtHtP, PtGtP and hybrid bulk electrical storage options.

	PtHtP	Hybrid	PtGtP
Electrical efficiency	High	Medium	Low
CHP efficiency	High	Medium	Low
Investment for power components	Low	Medium	High
Duration of storage	Daily	Daily and Weeks	Daily and Weeks

integration of high temperature molten salt storage is mainly given at the energy input and output of the process interfaces. On the input side, the hybrid process supply with fuel firing and electricity is already in use in some cases and offers a flexibility option for the electrical grid. With the help of molten salt storage, a larger share of volatile renewable electricity could be potentially converted to a steady high-temperature heat stream. Hence, molten salt storage could further increase the share of volatile electricity. In addition, there are options for molten salt storage integration for heat recovery at the process waste heat streams of batch processes or for temporal decoupling of processes.

In conventional power plants, molten salt storage could be installed to a different extent in the future. Small sized molten salt systems could increase the flexibility of the plants. Medium sized storage systems could be charged with volatile PV and wind electricity and operate in hybrid mode with fossil fuel combustion and volatile electricity supply. Also, the potential of full conversion or reuse of conventional coal power plants to power-to-heat-to-power (PtHtP) systems or newly erected PtHtP systems with large-sized storage systems is feasible. Furthermore, there are several

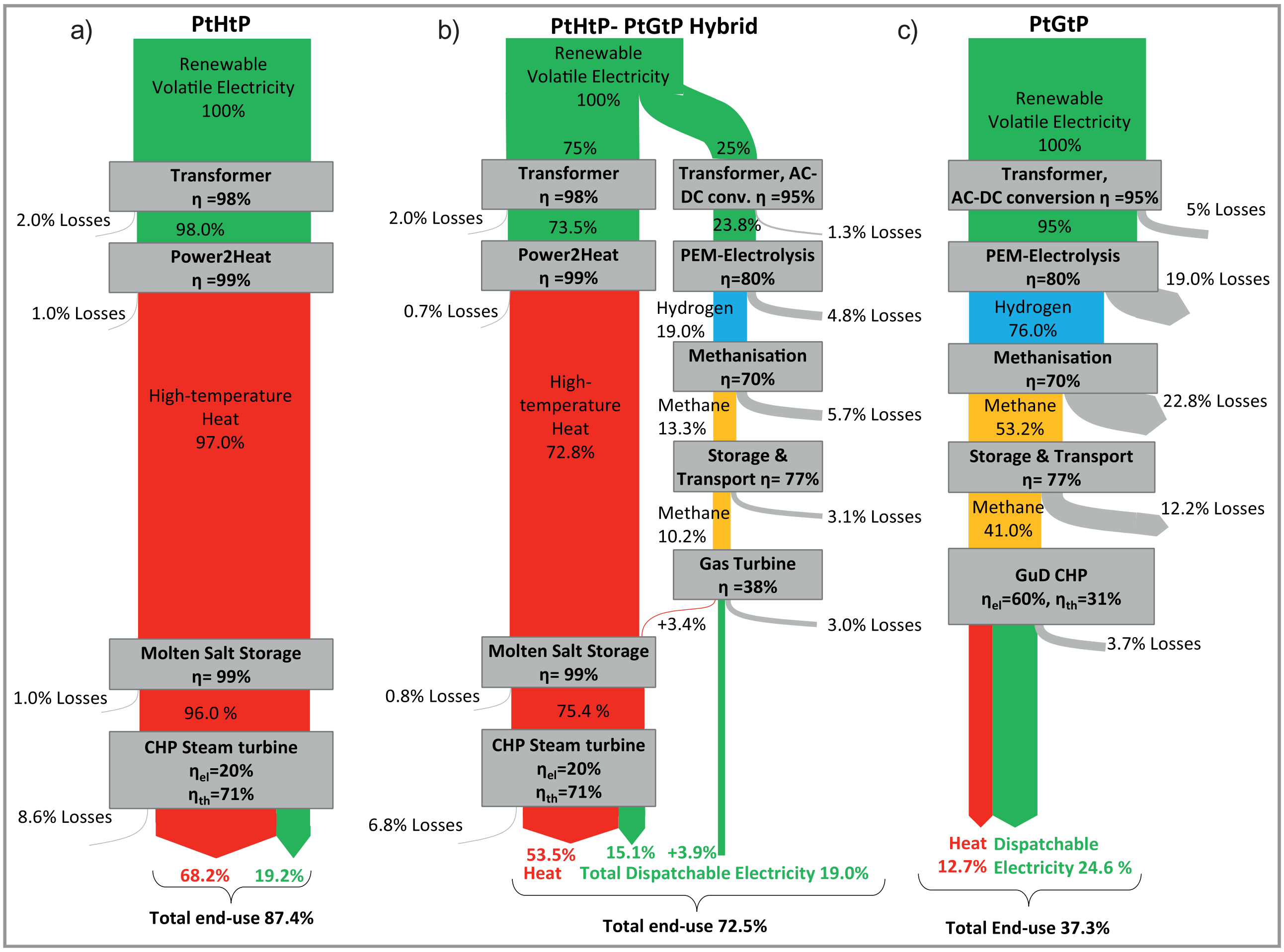

Figure 6. Energy Sankey diagrams of bulk electrical storage options: power-to-heat-to-power (PtHtP) storage (a), hybrid storage with an arbitrarily ratio of 75% power-to-heat and 25% power-to-gas (b) and Power-to-Gas-to-Power (PtGtP) storage redrawn from Ausfelder (c) (Source: DLR).

innovative electrical storage configurations with molten salt storage with the potential of higher efficiencies under investigation. They include pumped thermal energy storage (PTES), liquid air energy storage (LAES) and adiabatic compressed air energy storage (A-CAES). In this article the hybrid configuration of PtHtP and power-to-gas-to-power (PtGtP) was proposed in order to combine the advantages of both concepts.

Hence, molten salt storage could not only be utilized in CSP but also new fields of application. Examples are industrial processes, conventional power plants and electrical storage. In order to realize molten salt storage systems within these new fields of application, research projects for first-of-its-kind demonstrations are required.

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Abbreviations

A-CAES	adiabatic compressed air energy storage
CAPEX	capital expenditure
CHP	combined heat and power
CSP	concentrating solar power
HTF	heat transfer fluid
TES	thermal energy storage
ETES	electrothermal energy storage (see also PtHtP)
LAES	liquid air energy storage
OPEX	operational expenditure
PTES	pumped thermal energy storage
PtH	power-to-heat
PtHtP	power-to-heat-to-power, or (see also ETES)
PtGtP	power-to-gas-to-power

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Molten Salt Storage for Power Generation

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Review: An overview of molten salt energy storage in commercial concentrating solar power plants as well as new fields for its application is given. With regard to the latter, energy-intensive industrial processes, conventional power plants, and bulk electrical storage sytems are discussed. ……………………………………………………………………… ■