PERSPECTIVE

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A perspective on high-temperature heat storage using liquid metal as heat transfer fluid

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Abstract

Energy storage systems are essential to secure a reliable electricity and heat supply in an energy system with high shares of fluctuating renewable energy sources. Thermal energy storage systems offer the possibility to store energy in the form of heat relatively simply and at low cost. In concentrating solar power systems, for instance, molten salt-based thermal storage systems already enable a 24/7 electricity generation. The use of liquid metals as heat transfer fluids in thermal energy storage systems enables high heat transfer rates and a large operating temperature range (100°C to >700°C, depending on the liquid metal). Hence, different heat storage solutions have been proposed in the literature, which are summarized in this perspective. Based on these, future technical advances are suggested such as reducing the liquid metal share in the heat storage, using waste material as storage medium or using liquid metal as heat transfer fluids not only in sensible, but in latent or thermochemical energy storage systems. The use of waste material in a packed bed configuration with 5% porosity, for example, can bring down the storage material costs to 2%–3% of the costs of a liquid metal-only storage system. Furthermore, future application fields beyond concentrating solar power are proposed: supply of industrial process heat, waste heat integration and power-to-heat-to-power processes.

KEYWORDS

high-temperature, liquid metal, packed bed, thermal energy storage

1 | INTRODUCTION

In December 2019, the European Commission published the European Green Deal with the goal of a climate-neutral EU in 2050. This puts the focus on the development of efficient, large-scale and cost-effective storage technologies that will enable renewable energy to be provided on demand in a controllable manner.

Besides battery storage, thermal energy storage systems are widely investigated for buffering the gap between energy demand and generation due to their general simplicity and low cost. For providing industrial process heat and for electricity conversion processes (heat-to-power), especially the use of high-temperature thermal energy storage systems is discussed. The technical solutions with the highest technology readiness levels are sensible energy storage systems based on molten salt systems, which are known from their use in concentrating solar power (CSP) plants.[1] However, the International Renewable Energy Agency (IRENA) states that until

2023, higher temperatures of 600°C–700°C.[2] in case of CSP and up to 1000°C in case of industrial use cases—in combination with higher efficiencies, lower costs and more cycles—need to be achieved.

As an alternative solution, liquid metal-based heat storage systems are proposed. Liquid metal thermal energy storage systems are capable of storing heat with a wide temperature range and have, thus, been investigated for liquid metal-based CSP systems[3,4] and in the recent past also been proposed for industrial processes with high temperature process heat.[5]

Up until now, only publications on theoretical and experimental investigations on individual storage concepts using liquid metals as heat transfer fluids have been published. This publication, by contrast, will give an overview of the state of the art of liquid-metal based heat storage and propose pathways to future advances and application fields. The perspective is focused on thermal energy storage systems using liquid metal as heat transfer fluids, but not necessarily as heat storage medium. For the latter, the interested reader is referred to several reviews available on latent heat storage systems using liquid metal as a phase change material.[6,7]

This perspective is structured as follows: First, candidate liquid metals are presented and discussed (section 2). Second, the state of the art of thermal energy storage is summarized (section 3). Third, future technological advances (section 4) and future application fields (section 5) are proposed and discussed, followed by concluding remarks (section 6).

2 | CANDIDATE LIQUID METALS

Advantages and limitations of liquid metals in comparison with conventional heat transfer fluids with focus on the application in CSP plants are presented by Pacio and Wetzel[8] and are summarized and adapted to the application in heat storage systems in the following. If compared with gaseous heat transfer fluids such as air or steam, liquid metals are advantageous regarding the efficiency of the heat transfer, but disadvantageous regarding costs and melting points above room temperature. Compared with liquid heat transfer fluids such as nitrate salts, the larger liquid temperature range of liquid metals is advantageous, however, higher material costs and a low specific heat capacity disqualify liquid metals for direct heat storage.

Table 1 presents the liquid temperature ranges from melting to boiling temperature of selected liquid metals. In order to be applicable to high-temperature heat storage, the selection criteria are a maximum melting point of 400°C, a minimum boiling point of 700°C and existing

TABLE 1 Temperature regions[8] and costs of candidate liquid metals, *commodity prices (commercial purity)[10,11] of April 2023, should only be considered as a rough order-of-magnitude approximation.

	T_{min} (°C)	T_{max} (°C)	Cost* (€/kg)
Alkali metals			
$Na_{22.2}K_{77.8}$	−12	785	2
K	64	766	2
Na	98	883	2
Li	180	1342	40
Heavy metals			
$Pb_{44.5}Bi_{55.5}$	125	1533	12
Bi	271	1670	20
Pb	327	1743	2
Fusible metals			
Ga	30	2237	550
In	157	2072	400
Sn	232	2687	23

operating experience. Because of the latter, cadmium and thallium are discarded. Mercury is also not considered because of these criteria, as it is liquid from −38.9°C to 357.3°C.[9] The selected liquid metals are grouped into alkali metals, heavy metals and fusible metals. Pacio and Wetzel[8] discuss the compatibility issues with structural materials and give a classification of structural material combinations with different liquid metals.

Among the alkali metals, which react exothermically with water, sodium (Na) shows a lower reactivity than potassium (K) and sodium-potassium (NaK)[12] and is the most abundant of the alkali metals.[13] Additionally, a lot of experience has been gained in handling Na in the nuclear industry. Therefore, it is the preferred alkali metal candidate in the literature. Eutectic sodium-potassium ($Na_{22.2}K_{77.8}$) has the advantage of being liquid at room temperature.

The heavy metals generally show higher boiling temperatures. Among the heavy metals, the eutectic mixture of lead and bismuth ($Pb_{44.5}Bi_{55.5}$ or LBE) has the lowest melting temperature. Lead (Pb) is interesting from a material cost perspective, as the costs are in the same range as for Na. Pb and its oxides are toxic when ingested, but due to its low vapor pressure, the risk can be minimized in closed-loop systems. For LBE, large experience exists from the use as coolants in advanced nuclear reactors.[14]

Among the fusible metals listed here, tin (Sn) is the only one that is interesting from an economic point of view, but has the highest melting temperature. It is being

TABLE 2 Thermophysical properties of candidate liquid metals for high-temperature thermal energy storage systems (at 600°C).[8]

	c_p, kJ/(kgK)	λ, W/(mK)	ρ, kg/m^3	μ, 10^{-3}Pas
Alkali metals				
Na$_{22.2}$K$_{77.8}$	0.87	26.2	750	0.18
K	0.76	34.9	705	0.15
Na	1.25	46.0	808	0.21
Li	4.16	49.7	475	0.34
Heavy metals				
Pb$_{44.5}$Bi$_{55.5}$	0.15	12.8	9660	1.08
Bi	0.15	16.3	9940	1.17
Pb	0.15	18.8	10 324	1.55
Fusible metals				
Ga	0.36	50.0	6090	0.77
In	0.24	47.2	6670	0.75
Sn	0.24	33.8	6330	1.01

used in the float-glass process in industrial glass production. Therefore, operational experience exists for stagnant liquid Sn.

Table 2 lists the thermophysical properties of the selected liquid metals. The alkali metals and the fusible metals show high thermal conductivities (λ). The alkali metals have comparable densities (ρ) to water, the fusible metals have an order of magnitude larger densities. Among the liquid metals, the heavy liquid metals possess the highest densities ($\approx 10^4$ kg/m^3), lowest heat capacities (c_p) and lowest thermal conductivities among the liquid metals.

Based on their liquid temperature range, their material costs and thermophysical data, Na, LBE, Pb, and Sn are the most promising liquid metals for the use in thermal energy storage systems and evaluations in section 4 will focus on these four metals.

3 | PAST WORK—A BRIEF OVERVIEW ON LIQUID METAL-BASED THERMAL ENERGY STORAGE

In this literature review, the works are split into heat storage systems using alkali metals, such as Na or NaK as heat transfer fluids and those using heavy liquid metals, such as Pb and lead-bismuth.

3.1 | Alkali metal based

As the first pilot-scale direct heat storage with Na, a two-tank configuration was installed in the IEA-SSPS facility in Almeria, Spain, in the 1980s. The storage system had a maximum temperature of 530°C and a storage duration of 2 h.[15] The same two-tank configuration with liquid Na has been installed in Jemalong, Australia, in a pilot-scale CSP plant, with a maximum temperature of 565°C and a storage duration of 2 h.[3]

Apart from that, only theoretical concepts have been proposed for alkali metal-based sensible heat storage systems. As an alternative for the application in CSP, a packed-bed heat storage with iron spheres in single or multiple tanks with Na as the heat transfer fluid was mentioned by Pomeroy in 1979.[16] In 2012, a single-tank concept with a floating barrier between the hot and the cold Na was proposed by Hering et al.[17] For the use as thermal energy storage systems in nuclear power plants, hexagononal steel structures were suggested to be used with Na as the heat transfer fluid by Forsberg.[18,19] A previous evaluation of the author regarding different storage solutions showed that, when using Na, a packed-bed thermal energy storage is a promising solution based on five evaluation parameters (storage medium cost, storage density, cycling behavior, technology readiness level, and suitability for Na).[20] In a subsequent comparative study, it was concluded that, besides small filler diameters and large tank height to tank diameter ratios, low porosities are advantageous, as they minimize the axial thermal diffusion processes in the packed bed.[21] In accordance with these findings, Coventry et al. proposed a low-porosity configuration consisting of magnesia bricks with narrow channels and presented an experimental design.[22] Additionally, a numerical study focusing on this low porosity configuration was performed showing the advantages of their system over the packed-bed system regarding the pressure loss at extremely low porosities <5%.[23]

Furthermore, latent heat storage systems in combination with alkali-metal heat transfer fluids have been suggested: A latent heat storage with aluminum silicon as storage material and NaK as heat transfer fluid has been proposed and evaluated conceptually by Kotzé et al.[24,25] As an innovative direct contact latent thermal energy storage, a combination of sodium chloride in contact with liquid Na was presented and theoretically investigated by Kee et al.[26]

3.2 | Heavy liquid metal based

For the application in a CSP plant with air as the heat transfer fluid in the receiver, a 21-kWh two-tank storage configuration with eutectic lead-bismuth ($Pb_{44.5}Bi_{55.5}$) as the storage medium was demonstrated with maximum temperatures of 770°C by CSIRO in 2015.[27] They concluded that the identification and availability of suitable material is still the key obstacle for the demonstration of a long term storage system. Within the framework of the H2020 project NEXTOWER, a Pb-based demonstrator SOLEAD was designed to be integrated into a 100 kW CSP plant that used air as the heat transfer fluid in the thermal receiver in 2020. The concept is a one-tank direct heat storage configuration with two integrated heat exchangers using liquid Pb as the storage medium at temperatures from 600°C to 750°C.[28] The storage tank was 1.2 m in diameter and 3.6 m in height. Complementary material tests of 800H steel with an FeCrAl coating in liquid Pb at 800°C showed sufficient resistance against the liquid metal.[29] The heat storage is planned to be installed at ENEA Brasimone in Italy for conducting material corrosion tests but not yet thermal stratification tests.[30] Experimental results are not yet published to the author's best knowledge.

At the Karlsruhe Liquid Metal Laboratory (KALLA) heavy liquid metals are also being studied for use as heat transfer fluids in heat storage systems. A previous numerical study by the author presents the advantages of heavy liquid metals. When compared with liquid Na and solar salt in a packed-bed storage, eutectic lead-bismuth showed the highest efficiencies during discharge/charge and standby.[31] In further numerical works, the cyclic and standby behavior of a storage system with lead-bismuth and a packed bed with varied filler parameters and properties was theoretically analysed.[32-34] Recently, a packed-bed storage system with eutectic lead-bismuth as the heat transfer fluid has been demonstrated on a lab-scale (1 kWh) at KIT. A packed bed of ceramic fillers (zirconium silicate) was used with temperatures of up to 380°C.[35] The results showed that such a system is feasible and performs more efficiently

than a single-medium thermocline storage tank with lead-bismuth only. Currently, a 100-kWh packed-bed storage system is under construction and will be integrated and tested in a test rig at KALLA at KIT. In parallel, material and component (pumps, valves, measuring devices) tests are being carried out at 700°C to identify compatible structural materials.

3.3 | Comparative summary of storage materials

In the literature, direct and indirect heat storage concepts using liquid metal as heat transfer fluids have been proposed. Tables 3 and 4 give a comparative summary of the storage materials used in the studies described in this chapter.

Table 3 shows that using liquid metals as direct heat storage result in lower storage densities (ρc_p) in comparison with solid storage material. In addition, the material costs are higher. This is why the next sections of this study concentrate on indirect heat storage solutions.

Using latent heat storage material (Table 4) can lead to higher storage densities by making use of the high melting enthalpies at the melting point. In the literature, aluminum silicon and sodium chloride have been proposed as phase change material for heat storage with liquid metals as heat transfer fluids.

4 | FUTURE ADVANCES IN LIQUID-METAL BASED THERMAL ENERGY STORAGE

Future improvements focusing on improving cost efficiency, storage efficiency, and storage density are suggested. This includes not only improving existing configurations but also new or combined concepts, which are also presented in the following.

4.1 | Reduction of liquid-metal share

Reducing the liquid metal content by using a solid storage medium in the thermal energy storage system has three main advantages: the overall storage medium costs can be reduced as the parts of the higher-priced liquid metal is replaced by a low-cost filler material.[21] at the same time the heat capacity of the storage can be increased and the safety measures can be minimized as only a small amount of liquid metal is in use.[22]

Compatible solid storage material for thermal energy storage applications have not yet been studied deeply in

TABLE 3 Storage materials proposed for heat storage concepts with liquid metals as heat transfer fluid. Data for liquid metals from Tables 1 and 2.

	c_p, kJ/(kgK)	ρ, kg/m^3	ρc_p, MJ/(m^{3}K)	Costs, €/kg
Direct				
Na[15]	1.25	808	1.0	2
Pb$_{44.5}$Bi$_{55.5}$[27]	0.15	9660	1.4	12
Pb[28]	0.15	10 324	1.5	2
Indirect				
Iron[16]	0.63	7880	5.0	0.1[10]
Steel[18]	0.45	7800	3.5	0.5
MgO[22]	1.23	3544	4.4	0.9
ZrO$_2$-SiO$_2$[35]	1.28	4204	5.4	11.7

TABLE 4 Latent energy storage materials proposed for heat storage concepts with liquid metal as heat transfer fluid.

	Melting enthalpy (kJ/(kg))	Melting point (°C)	Costs (€/kg)
AlSi$_{12}$[24]	560	576	2.2
NaCl[26]	496[36]	801	n.a.

the literature. Therefore, for this cost-related study, magnesia is chosen, which is proposed by Coventry et al.[22]

The costs of the packed-bed storage material in €/kWh (thermal) can be calculated according to Equation 1 (l = liquid, s = solid).

$$\text{cost} = \frac{\rho_l \cdot \varepsilon \cdot \text{cost}_l + \rho_s \cdot (1-\varepsilon) \cdot \text{cost}_s}{(\rho_l \cdot c_{p,l} \cdot \varepsilon + \rho_s \cdot c_{p,s} \cdot (1-\varepsilon)) \cdot \Delta T} \quad (1)$$

It has to be noted that this is only taking into account the storage material costs, assuming that the other costs associated with the heat storage system are similar among the liquid metal-based systems that are compared in this study. At high temperatures, the additional costs for tanks, heat exchanger, piping, insulation, etc. are expected to be in the same range as the material costs or even higher. For instance, previous publications estimate 34% (molten salt two-tank),[37] 56% (molten salt two-tank),[38] or 43% (molten salt thermocline with quartzite)[38] of the total costs for the storage material. Another cost evaluation[39] gives lower numbers of 14% (molten salt thermocline with limestone) and 18% (structured thermocline with concrete) for the storage material costs, but also take into account additional costs such as sales tax, construction, and engineering costs.

The heat capacity can be determined in relation to either the volume (Equation 2) or the mass (Equation 3) of the storage material.

$$C_V = (c_{p,l} \cdot \rho_l \cdot \varepsilon + c_{p,s} \cdot \rho_s \cdot (1-\varepsilon)) \cdot \Delta T \quad (2)$$
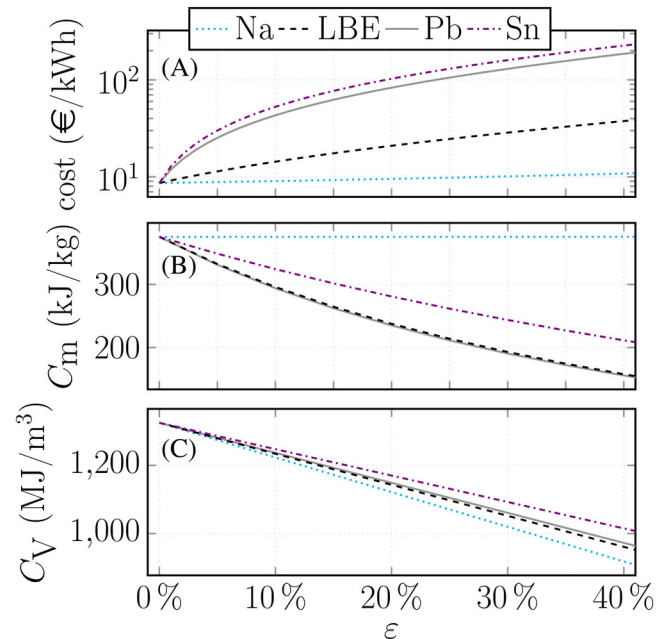
FIGURE 1 Influence of reducing the liquid metal share (decreasing the porosity) in a MgO packed bed for sodium (Na), lead-bismuth eutectic (LBE), lead (Pb), and tin (Sn) regarding (A) storage material costs, (B) mass-specific heat capacity, and (C) volume-specific heat capacity.

$$C_m = \frac{c_{p,l} \cdot \rho_l \cdot \varepsilon + c_{p,s} \cdot \rho_s \cdot (1-\varepsilon)}{\rho_l \cdot \varepsilon + \rho_s \cdot (1-\varepsilon)} \cdot \Delta T \quad (3)$$

The results for low porosities from 0 to 0.4 are shown in Figure 1 for four liquid metals (Na, LBE, Pb, and Sn).

Filler	Costs (€/kg)	ρ (kg/m³)	c_p (J/kgK)	ρc_p (MJ/m³K)
Cofalit®	0.008	3120	860	2.7
MgO	0.9	3544	1231	4.4

TABLE 5 Storage material costs and physical properties of potential storage materials (a waste product and magnesia).[22,62]

The values are exemplarily calculated with the costs and properties for magnesia (MgO) as storage material (Table 5), a temperature difference of 300 K and liquid metal properties at 600°C (Table 2).

Figure 1A) illustrates that the storage material costs decrease significantly with decreasing amount of liquid metal in the heat storage with theoretical minimum storage costs of 8.6 €/kWh for $\varepsilon = 0$. This only represents the solid storage material costs (in this case MgO) and is therefore highly dependent on the storage material chosen. For a low amount of liquid metal ($\varepsilon = 5\%$), the costs are 8.8 €/kWh for a Na-based, 11.4 €/kWh for a Pb-based, 25.3 €/kWh for a LBE-based, and 30.1 €/kWh for a Sn-based heat storage. The Na and the Pb-based packed-bed storage system are in the range of 15 €/kWh, which is proposed by the Strategic Research Agenda 2020–2025 of the European Solar Thermal Electricity Association[40] as maximum investment costs for the overall storage system.

Figure 1B,C show an increase in the heat capacity of the storage when using less liquid metal in the packed-bed storage. In the case of liquid Na, the specific heat capacity c_p is comparable with that of magnesia and thus, no improvement can be achieved with regard to the amount of energy stored per mass (C_m). However, due to the low density of Na compared with magnesia, the energy stored per volume can be significantly increased.

A previous study[21] showed that, due to its excellent heat transfer capabilities, a small amount of liquid metal in a low porosity packed structure still transfers heat efficiently compared with using molten salts. The heat storage is indeed even more efficient at low porosities, as the axial thermal diffusion effects are minimized by the high content of solid filler material. For molten salts, by contrast, this is not the case due to comparatively lower thermal conductivities. Thus, for molten salts, the filler material is only advantageous with regard to storage material costs.

Among the liquid metals in this study, the use of Pb and lead-bismuth as heat transfer fluids is expected to reach higher discharging/charging efficiencies than with using Na because of the comparably lower thermal conductivity, which leads to a smaller thermocline region while maintaining excellent heat transfer to the packed bed. This is explained in detail in a previous publication.[31] Sn having thermophysical properties between those of Na and Pb/lead-bismuth is expected to show efficiencies in between.
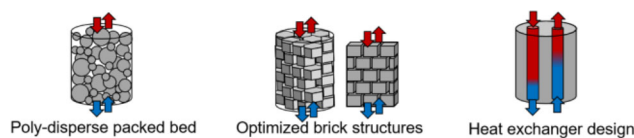

FIGURE 2 Three possibilities to realize a minimium liquid metal share in a heat storage with liquid metal acting mainly as the heat transfer fluid.

Bozorg et al.[23] presented the advantages for even lower porosities (5%) in a rectangular tank and square solid bricks. As expected, the liquid metal behaved better than a model fluid with 10 times lower thermal conductivity during discharge/charge.

How can we realize a minimum liquid metal amount in a thermal energy storage? Possible technical solutions are schematically shown in Figure 2 and discussed in the following.

First, low porosities in a heat storage system can be achieved by using polydisperse packed beds with varying filler material sizes. Minimum values of 22% are reported in the literature.[38,41,42] In such a configuration, large heat transfer surfaces can be achieved by using spherical particles. However, in packed beds, the issue of thermal ratcheting is of concern, which may result in plastic deformation of the tank during charging and discharging. If the expansion of the tank is larger than that of the filler material during charging, the particles rearrange in the gap formed between the tank wall and the packed bed. In the subsequent discharge cycle, the tank is then unable to contract to its original shape, leading to a ratcheting effect of multiple cycles.[43,44]

Another possibility is to use geometrically optimized structures that leave only channels for the liquid metal to flow through, as is for example, planned by Coventry et al.[22] They claim that lower porosities can be achieved in their thermal energy storage system compared with a packed bed configuration. Furthermore, due to their rectangular tank design thermal ratcheting can be avoided. Another possibility would be to apply optimized geometries, for example, honeycomb-shaped or otherwise structured filler material suitable for cylindrical tanks, which are used in hot blast stoves[45] but which have not yet been proposed and tested for liquid-metal based storage systems to the best of the author's knowledge.

If we think further in the direction of using liquid metals primarily as a heat transfer medium and not as a

storage medium, an arrangement, in which liquid metal is pumped through tubes in a heat exchanger to transfer the heat to a storage medium, could be a promising option, as for example, proposed by Kotzé et al.[25] The storage medium could be either a sensible (e.g., solids or molten salts), a latent (e.g., salts or metals) or a thermo-chemical heat storage medium. This allows for complete decoupling of heat transfer and heat storage. Moreover, there is no direct contact and no corrosion issues between the two media, so only the structural material of the tubes needs to withstand both media. However, in this configuration, the heat transfer surface is the smallest of the proposed solutions and can be improved for example, by using fins, as is already done for latent heat storage systems with molten salt phase change material,[46] or using a storage medium with high thermal conductivity (e.g., molten metal as phase change material).[47]

The future work should focus on configurations with a minimized amount of liquid metal in the storage system. Examples have been proposed in the literature, but a techno-economic optimization should be performed.

4.2 | Increase of heat storage density

An increase of the heat storage density leads to two improvements: a heat storage system can be discharged for a longer period of time and the storage material costs relative to the stored energy (in €/kWh) are reduced.

How can we increase the heat storage density of our heat storage system assuming a sensible thermal energy storage system to start with? It can be improved by one or more of the following options that are depicted in Figure 3.
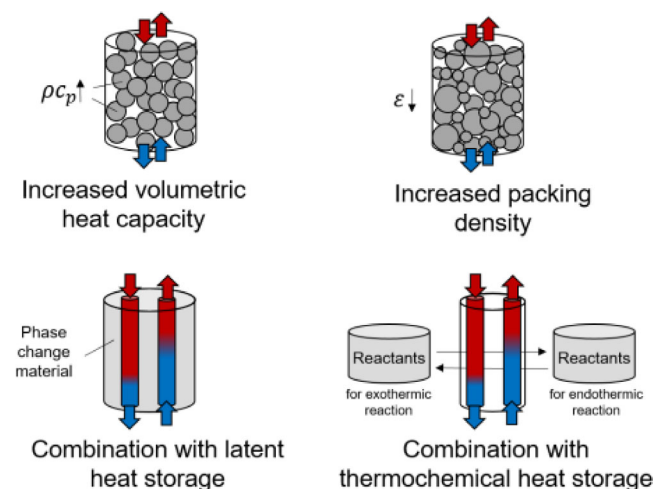

FIGURE 3 Schematics of configuration possibilities for increased heat storage density.

In the literature, ceramic materials, such as alumina and magnesia, and metallic materials, such as cast iron and pure iron, are proposed as storage materials with high heat capacities of >3 MJ/(m³K).[48]

With a higher storage capacity, a longer discharge of the packed-bed storage can be realized assuming a fixed discharge power.[34]

The increase of the packing density could be achieved by either a poly-disperse packed bed or optimized geo-metrical structures, as discussed in section 4.1.

First theoretical investigations and lab-scale proto-types already proposed the use of a latent thermal energy storage system with liquid metal as the heat transfer fluid (section 3). Possible configurations using liquid metals as heat transfer fluids could be either an encapsulated packed-bed,[49] a heat exchanger (finned-tubes) concept,[46] or an active system with a moving heat transfer surface.[50] However, for these configurations, lab- to pilot-scale demonstrations and the identification of ideal material combinations, especially for temperatures >300°C, are still missing and should be the next steps regarding this work.

The combination of liquid metal as heat transfer fluid with a thermochemical heat storage system has not been reported yet but would combine efficient heat transfer with a high heat storage density.

4.3 | Reduction of storage material costs

Waste or by-products from industrial processes are pro-posed as thermal energy storage materials in order to fur-ther bring down storage material costs. For heat storage systems with molten salt, materials are already studied and tested,[51,52] however, not yet for the application in liquid-metal based systems to the best of the author's knowledge. For their use in a heat storage system using liquid metal as heat transfer fluid, the chemical compati-bility and the applicability for high temperatures and a high thermal shock resistance has to be tested first.

In the literature, various waste materials are studied: ceramics from conditioned asbestos-containing waste,[53] fly ashes,[51] by-products from the mining and metallurgi-cal industry[54-57] or from potash industry[58] and demoli-tion waste.[59] Gutierrez et al.[60] provide an overview of waste and by-product material in thermal energy storage systems. A more recent review of Jacob et al.[61] focusses on waste material for high-temperature heat storage (200°C–750°C).

The material costs of the waste and by-products in this study are ranging from 0.001 to 0.2 €/kg.[57,60,61] This is one to five orders of magnitude lower than the material costs of liquid metal (Table 1). Therefore, a low-porosity packed

TABLE 6 Exemplary storage material costs reduction with magnesia and waste product fillers in a packed bed with a porosity of $\varepsilon = 22\%$, 5%, and 1% in €/kWh.

ε	Filler	Na	LBE	Pb	Sn
100%	No filler	24.7	1020.9	167.2	1009.1
22%	MgO	9.6	91.9	22.3	113.6
22%	Cofalit®	2.5	131.4	22.6	163.3
5%	MgO	8.8	25.3	11.4	30.0
5%	Cofalit®	0.6	27.4	4.8	35.2
1%	MgO	8.7	11.9	9.2	12.8
1%	Cofalit®	0.2	5.5	1.0	7.0

bed system with a high content of low-cost filler material can reduce the overall storage medium costs significantly.

An exemplary calculation with the material Cofalit®, which is a waste product from the industrial vitrification of asbestos and which has a storage material cost of 0.008 €/kg,[62] illustrates the possibilities in cost reductions with waste material. The material costs and physical properties are shown in Table 5 in comparison with magnesia (MgO).

The storage medium cost in €/kWh of a packed-bed storage with liquid heat transfer fluids are determined according to Equation 1 using the physical properties and cost data of Tables 1–5. The porosity ε is set to three reference values: 22%, as this has been achieved in previous experiments with poly-disperse packed beds,[38] 5%, as this was proposed for a structured packed-bed arrangement in the literature,[22] and 1% to show the theoretical cost reductions that are possible with a further increase of the waste material fraction in the heat storage. The temperature difference ΔT is set to 300 K, for example, from 400°C to 700°C.

The results in Table 6 show that, if using waste material as a storage medium, the costs can be reduced to 9%–39% of the costs of a liquid metal-only storage system given that a porosity of 22% is achieved. The cost reduction is maximum when using liquid Na (39%) resulting in material costs of 9.6 €/kWh. In case of Pb a reduction of 13% results in 22.3 €/kWh.

For porosities of 5%, the costs can be brought down to 2%–3% of the liquid-metal only storage system. In the case of Na, that means 0.6 €/kWh and in the case of Pb, it is 4.8 €/kWh. The waste product material shows its cost advantages only in combination with the liquids Na and Pb due to its lower heat capacity (ρc_p) when being compared with MgO (Table 5).

The storage material costs at $\varepsilon = 1\%$ show the potential to further bring down the costs to 0.2 €/kWh (Na)–7.0 €/kWh (Sn).

Additional to the cost reduction, the storage density can be increased in comparison with a liquid metal-only solution, for which ρc_p is only ranging from 1.0 to 1.5 MJ/m³K (see Table 2). This is leading to longer discharge times assuming a constant discharge power.

All in all, the use of waste material shows a large material cost reduction potential, however, the compatibility of the waste materials with liquid metal needs to be proven.

5 | FUTURE APPLICATION FIELDS OF LIQUID-METAL BASED HEAT STORAGE BEYOND CSP

In the past, thermal energy storage systems using liquid metals have for the most part been investigated for the use in CSP systems, where liquid metals show high heat transfer coefficients in the thermal receiver, first in the 1980s and then again recently in the so-called generation 3 (Gen3) CSP plants.[63] This section focuses on application fields beyond that, in which heat storage systems become more and more important and in which also liquid-metal based heat storage can play an important role in the future.

5.1 | Integration of a liquid-metal based heat storage for process heat supply for high-temperature industry

In industrial processes, a large amount of energy is needed in the form of process heat with more than 33% for high-temperature processes above 500°C, for example, in the chemical industry and in the metal and glass manufacturing.[64] Thermal energy storage systems can help the decarbonization of industrial process heat supply allowing to include fluctuating renewable energy sources and at the same time providing energy security with heat on demand.[65] Figure 4 shows such a schematic power-to-heat (P2H) process.
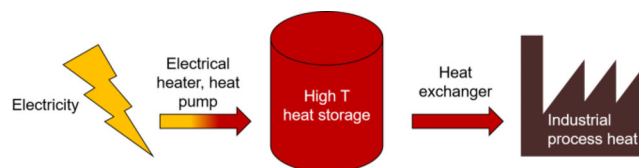
FIGURE 4 Integration of a high-temperature heat storage in a P2H system for the supply of high-temperature industrial process heat.

5.2 | Storage of waste heat with a liquid-metal based heat storage for high-temperature industry

In energy-intensive industrial processes, large amounts of waste heat are generated. Miró et al.[66] list industrial waste heat shares from 9.1% to 22.2% compared with the overall energy consumed by the industry in the EU. This is in accordance with a study by Papapetrou et al.[67] that specifies a waste heat potential of 304 TWh/year in the EU. This represents 16.7% of the industrially consumed process heat and 9.5% of the total industrial energy consumption. They state that waste heat temperatures of 500°C–1000°C occur, for example, in the steel industry with a large recovery potential of 124 TWh/year. For those temperatures, liquid metals could efficiently transfer the heat from the waste heat source, which is usually in the form of hot gas, via a heat exchanger to a heat storage medium (e.g., solids).

Figure 5 illustrates a schematic integration of a heat storage using waste heat from industrial processes. The stored heat can then be used for other high-temperature processes.

5.3 | Use of a liquid-metal based heat storage in P2H2P systems

Another promising possibility is the use of thermal energy storage systems in power-to-heat-to-power (P2H2P) systems, for example, in so-called Carnot batteries.[68] Figure 6 shows a scheme of a possible configuration.
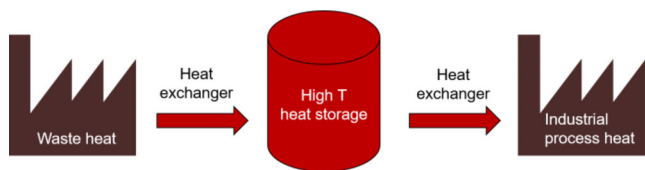

FIGURE 5 Integration of a high-temperature heat storage for using waste heat to supply of high-temperature industrial process heat.
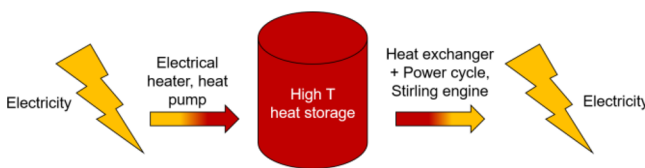

FIGURE 6 Integration of heat storage in a P2H2P system.

These systems are already demonstrated on a demo scale with round-trip efficiencies of 25%–77%.[69] Currently, solids, molten salts, water and phase change material are the prevailing materials in the thermal energy storage. The charging of the heat storage (P2H) of the currently demonstrated Carnot batteries is realized via resistance heaters or heat pumps. For the discharge process (H2P), steam, organic and CO_2 Rankine cycles, Brayton cycles or Stirling engines are used.[69] In comparison with gases as heat transfer fluids, the use of liquid metals in the heat storage system enables an efficient heat transfer to a secondary medium in the power cycle, for example, gas or steam. And in comparison with liquid heat transfer fluids such as molten salts, the heat transfer can take place at high temperatures (>600°C) allowing a conversion to electricity with high H2P efficiencies.[68]

As one possible application field the conversion of decommissioned coal-fired power plants into thermal storage plants is discussed in the literature, with the most costly part—the H2P conversion system—being already installed.[69]

6 | CONCLUSION

This perspective aims to present the state of the art in liquid-metal based heat storage systems, proposes pathways to future technological improvements in storage configurations and materials, and suggests application fields beyond CSP.

In the literature, mainly alkali-metal (Na, NaK) and heavy-metal (Pb, LBE) based heat storage systems are proposed. Configurations range from sensible direct systems (two-tank) to sensible indirect systems (packed bed) and latent indirect systems.

The following technical advances in future storage systems are proposed:

- The amount of liquid metal share needs to be reduced in order to reduce the overall storage medium costs, to increase the heat capacity and to minimize the required safety measures. This can be achieved by using extremely low porosities. Exemplarily, the costs for a packed bed with 5 vol% Na and 95 vol% magnesia can be brought down to 10.2 €/kWh compared with 24.7 €/kWh for a Na-only system. For further cost and efficiency optimization, further compatible filler materials need to be tested in contact with liquid metals.
- The heat storage density needs to be increased, for example, by choosing either a larger amount of filler material or filler material with higher specific heat capacities. A further improvement of the heat storage

density could be achieved by using latent or thermo-chemical heat storage systems.

- The storage material costs need to be reduced. This could be achieved by using waste material, for example, Cofalit, a waste product from the industrial vitrification of asbestos. With that material, the costs of a packed bed with $\varepsilon = 5\%$ and Na as the heat transfer fluid can be reduced to 0.6 €/kWh (for Pb: 4.8 €/kWh).

Following fields of application for liquid metal-based heat storage are proposed for the future:

- High-temperature heat storage with liquid metals can contribute to provide reliable industrial process heat >500°C from renewable (excess) electricity via power-to-heat processes.
- Liquid metals can also be used to efficiently transport high-temperature waste heat from high-temperature industrial processes to a heat storage medium for later use.
- Another promising application is the use in power-to-heat-to-power systems, for example, in so-called Carnot Batteries. The high heat transfer rates and high possible operating temperatures could allow for efficient electricity production.

NOMENCLATURE

l	liquid
m	mass specific
max	maximum
min	minimum
s	solid
V	volume specific
CSP	concentrating solar power
KIT	Karlsruhe Institute for Technology
KALLA	Karlsruhe Liquid Metal Laboratory
c_p	specific heat capacity (Jkg^{-1}K^{-1})
C_m	mass-specific heat capacity (kJ/kg)
C_V	volume-specific heat capacity (MJ/m^3)
T	temperature (K)
ΔT	temperature difference (K)
ε	porosity (%)
λ	thermal conductivity (Wm^{-1}K^{-1})
μ	dynamic viscosity (Pas)
ρ	density (kgm^{-3})

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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