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Opportunities of High-Temperature Thermal Energy Storage Technologies in the Process Industry

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Since many years, thermal energy storage (TES) technologies such as regenerator storage for hot gases and Ruths storage for steam have been state-of-the-art in the high-temperature process industry to improve the energy efficiency. Over the last years, some novel TES technologies became pre-commercial or commercial such as molten salt storage. At the same time there is a growing share of affordable but volatile electricity from PV and wind energy which leads to changes in the electricity market. Especially in the energy intensive industrial process heat sector, there are emerging topics like process hybridization with fossil and electrical supply, transition to flexible processes and storage options. Hence, integration of known and new high-temperature TES technologies in industrial processes is a field of growing importance.

Potential of high-temperature thermal energy storage usage in the process heat sector

In 2012 the industrial process heat consumption by end-use in the EU28 accounted for about 7300 PJ. The largest amount of this industrial process heat is high-temperature demand (5400 PJ with temperatures above 100 °C). In the future, a decarbonized process industry could be achieved by supply of synthetic gases and electricity [1]. For the latter a continuous development of power-to-heat (P2H) technologies is required. This allows for an intensified coupling of the electrical grid with high-temperature industrial processes and thus leads to improved integration of renewable energies. Though significantly increased contributions of renewable energy to the system load are expected, their volatile nature (e.g. wind and PV) still represents a barrier to a broader exploitation. High-temperature TES technologies are an option to balance the volatile renewable energy supply and a rather constant industrial process heat demand [2]. Major advantages of TES technologies compared to other energy storage options typically include low investment costs, independency of location, high efficiency, cycling stability and maturity [3].

There are different tasks and application areas for high-temperature TES utilization in the process heat sector:

- Thermal batch processes with cycles and utilization/integration of waste heat
- Temporal mismatch between the supply and demand of energy
  (or in other words balancing of discontinuous heat demand or supply)
- Local mismatch between the supply and demand of energy
- Reduction of part load operation
- Reduction of capital investments for the supply of peak loads
- Reduction of start-up and shut-down losses
- Supply of backup power
- Decoupling of heat and power supply for combined heat and power (CHP) systems

The following text gives an overview of high-temperature TES technologies. Fundamental principles, commercial technologies and R&D efforts in the field are presented.

Fundamental principles of thermal energy storage technologies

There are various ways to describe and classify thermal energy storage (TES) materials and systems. Most commonly three types of TES systems are distinguished:

- Sensible heat storage results in an increase or decrease of the storage material temperature; stored energy is proportional to the temperature difference of the used materials. Sensible heat can be stored in solids, liquids or solid-liquid mixtures.
- Latent heat storage is associated with a phase transformation of the storage materials (or phase change materials - PCMs), typically changing their physical phase from solid to liquid and vice versa. The phase change is always coupled with the absorption or release of heat and occurs at a constant temperature. Thus, the heat added or released cannot be sensed and appears to be latent. Stored energy is equivalent to the heat (enthalpy) of fusion.
- Thermochemical heat storage is based on reversible thermochemical reactions or sorption. The energy is stored in the form of chemical compounds created by an endothermic reaction and is recovered again by recombining the compounds in an exothermic reaction. The heat stored and released is equivalent to the heat (enthalpy) of reaction. This chemical compounds can be stored over long periods without thermal losses.

A characteristic of TES systems is that they are diversified with respect to storage principle, the temperature level, the energy density and maturity (Fig. 1). Additional important parameters (not shown) are the power and capacity values, the heat transfer fluid and the number of charge/discharge cycles per year [3].

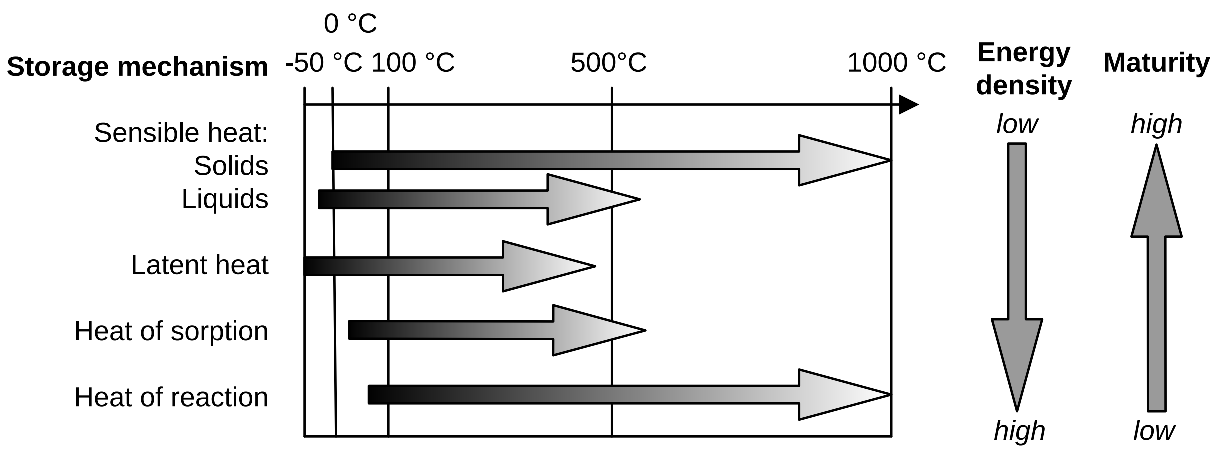

Fig. 1: Thermal energy storage mechanism, their working temperature, and correlation to energy density and status of technical maturity.

Overview of commercial high-temperature thermal energy storage technologies

Sensible heat storage in solids – Regenerator

During the charging and discharging process, solids alter their sensible temperature and the heat is stored or released through a temperature change. This storage type allows the highest storage temperature levels of up to 1600 °C, avoiding the problem of high vapor pressure of liquid media. The maximum application temperature depends on the specific material. Ceramics are typical utilized. Also, in spite of their relatively low specific heat, these – typically inorganic – solids may still achieve high storage densities, where the operating conditions exhibit large temperature spreads. This is often the case with applications that use gases as heat transfer fluid.

Today, heat storage in solid media is commercially applied in regenerative heat exchangers, also called regenerators. This storage type comprises a storage inventory that is heated and cooled through an intermittent heat transfer between a hot and a cold fluid. The storage is operated in counterflow: during charging, the hot fluid enters the storage module at the ‘hot’ end and during discharging the flow direction is reversed and the cold fluid enters at the ‘cold’ end.

Existing industrial examples include solutions in the steel industry, the glass industry, and industrial air purification systems. The steel industry was one of the earliest applications. Until today so-called hot blast stoves or Cowper stoves, to preheat the blast of a steel furnace are commercially utilized. To provide heat over a longer time period, two or three stoves are used in an alternating operation (see Figure 2). Sintered refractory bricks in hexagonal shape are a common inventory choice. The temperature in the upper part of the stove can be as high as 1300–1600 °C. Heat rates are in the range of 100 - 300 MW [4]. Regenerative thermal oxidizer (RTO) systems are applied to purify air from volatile organic compounds through an exothermic process taking place inside the regenerator unit. This process oxidizes the organic solvents at elevated temperatures in the range of 800 – 1000 °C. The internal heat transfer between the hot cleaned gas and the incoming cold gas is achieved through the intermittent storage of the heat in the regenerator’s ceramic inventory, allowing an almost autothermal plant operation with heat recovery efficiencies of up to 95 % and more. Commercial implementations of RTO have a typical volume of up to 600 m³ [4].

Fig. 2: Photo of a regenerator (or Cowper) for sensible heat storage in solids (Source: Paul Wurth).

Sensible heat storage in liquids – pressurized water

State of the art for the thermal storage used in process heat applications is the **steam accumulator** technology (also called the “sliding pressure water storage” or “Ruths”). Steam accumulators are charged by condensation of steam fed into the pressurized liquid volume. During the discharge process the pressure in the storage vessel is decreased and saturated steam is extracted. Since water is used both as a storage medium and heat transfer fluid, high discharge rates and short reaction times are possible (Fig. 3). Hence, buffer storage operation with a high thermal power is feasible.

Steam accumulators use sensible heat storage in pressurized saturated liquid water and the capacity is defined by the volume of the pressure vessel. The storage capacity corresponds to the variation of sensible energy of the liquid volume. While a larger decrease of pressure is advantageous regarding the volumetric storage capacity, the acceptable pressure variation might be limited by efficiency considerations and process requirements. The maximum operation temperature is limited by the critical point of saturated water (374 °C, 221 bar). The costs are dominated by the pressure vessel. Hence, typical systems operate at a maximum temperature of 250 °C with an upper pressure limit of 40 bar [5, 6].

Ruths storage systems can equalize and cover variation of steam or pressurized water demand or supply. Steam accumulator may supply heat to industrial steam grids, cover peak power, supply batch processes, or being used in combination with steam turbines or cogeneration. There are several processes which employ steam accumulators, such as in the mineral, pulp and paper, food, textile and chemical industries.

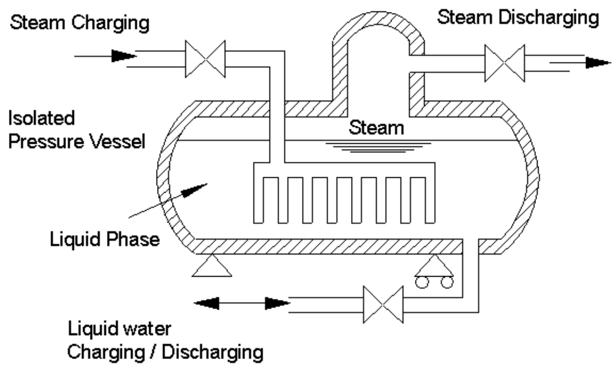

Fig. 3: Scheme of a steam accumulator for sensible heat storage in pressurized water.

For pressurized water also “**displacement storage**” or “thermocline” storage systems can be utilized. Hot and cold water are within one vessel. The hot less dense water is in the upper part, whereas the cold water is in the lower part. A temperature transition zone will form between cold and hot part. This zone will move up and down during charging and discharging. The outlet temperature will stay practically constant almost until the end of the discharge. In order to achieve good stratification, preferably a high vertical cylindrical vessel is utilized. Typical displacement storage supply pressurized water up to 180 °C (about 30 bar). Large-scale displacement storage systems are commercial products in the district heating sector [5].

Sensible heat storage in liquids - Molten salt

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. Nitrate salts known from the fertilizer application, are used as a storage medium. These salts are solid at room temperature and liquid at higher temperatures. High-temperature properties are similar to water in terms of the volumetric storage density, viscosity and transparency. The major advantages of molten salts are low costs, high thermal stabilities and low vapor pressures. The low vapor pressure results in storage designs without pressurized vessels (Fig. 4). In general there is experience with molten salts from a number of industrial applications related to heat treatment, electrochemical reactions and heat transfer. The application of salts requires the consideration of the lower temperature limit defined by the melting temperature. One aspect with molten salts is unwanted freezing during operation. Freezing must be prevented in the piping, the heat exchanger and in the storage tanks. Hence, often auxiliary heating systems are installed. The thermal stability of the molten salts defines the upper temperature limit. Salt mixtures, rather than single salts, have the advantage of a lower melting temperature. These mixtures can have similar thermal stability limits as the single salts of the mixtures. Hence, salt mixtures can have a larger temperature operation range compared to single salts. For solar thermal power plants (also called “concentrating solar power” - CSP plants), alkali nitrate salt mixtures are the preferred candidate fluids for TES. Typically a non-eutectic salt mixture of 60 wt% sodium nitrate and 40 wt% potassium nitrate is utilized. This mixture is commonly called Solar Salt. The minimum operation temperature of Solar Salt is typically set to 290 °C (limited by the liquidus temperature of about 250 °C). The maximum operation temperature is 560 °C defined by the thermal stability. The TES system consists of a cold (e.g. 290 °C) and a hot (e.g. 560 °C) unpressurized tank. For a temperature difference of 250 K, the storage density of the medium reaches a value of about 200 kWh/m³. Currently there are commercial solar thermal power plants with molten salt storage units up to 5000 MWh (Solana from Abengoa in the US). In 2015, the installed molten salt storage capacity in CSP plants was larger than 30 000 MWh and the grid-connected molten salt storage power, expressed as electrical power, was 1500 MW_{el}. For the CSP application, typical storage capacities range from 3 h to 15 h. At the time of writing, typical storage costs range from 20 – 75 €/kWh depending on parameters such as capacity and power, as well as the temperature difference between hot and cold tank.

Fig. 4: One tank of a two tanks molten salt system in a solar thermal power plant.

Overview of R&D high-temperature thermal energy storage technologies

Some of the high-temperature TES technologies are still in a research and development stage and undergo a continuous development. Some of them have already reached a pre-commercial level. The following text distinguishes between four different technological principles.

Sensible heat storage in solids

A wide choice of materials is usable and can provide economically attractive solutions [4]. In principle, any suitable candidate material that is chemically and thermally stable in the temperature range of interest can be used. Material options include various oxide ceramics, concrete, metals, graphite and – for particularly cost-effective solutions – also natural stones, such as basalt, or recycled waste materials such as vitrified fly ash [4, 7-11].

In recent years there has been increased interest in regenerator-type storage for various power plant applications, including combined cycle (CC) plants [7], concentrated solar power (CSP) plants [11] and adiabatic compressed air energy storage (ACAES) plants [10] for utility-scale electricity storage. In this context, the technology has been further developed for increased performance and lower costs. In particular regenerator storage based on a packed bed inventory has been looked at. It is less common today, but can further reduce investment costs and can avoid the scalability issues of previous designs. However, the design of large packed beds is afflicted with technical uncertainties related to thermomechanical aspects, in particular with a utility-scale deployment in mind [4]. These challenges have been tackled with the elaboration of novel calculation methods [12], design studies [7-11] and experimental tests in pilot scale (Fig. 5). To come to particularly cost-effective solutions, the use of specific natural stones, such as basalt, has been considered [7, 11].

Besides concepts with direct contact between the heat carrier (gas) and the storage medium, it can be in some applications attractive to have an indirect contact between heat carrier and storage medium. This would allow for the utilization of other heat transfer fluids than gases such as thermal oil or steam for regenerator type storage systems. In this case the use of concrete with an embedded metallic tube register is a favorable option. As a heat carrier thermal oil, pressurized water or pressurized steam can be used. Heat is then transferred from the heat carrier fluid through the pipe walls to the concrete acting as a sensible heat storage medium. The concept was demonstrated in a scale of 400 kWh at 400 °C with over 10000 operation hours by DLR [13, 14].

In a modular approach, the so-called CellFlux concept uses a heat exchanger, an intermediate closed fluid cycle (such as air) with a regenerator storage system. The heat exchanger provides the thermal power and the regenerator size corresponds to the capacity demand. This concept can be adapted to different primary heat carriers such as thermal oil or steam and can thus be used in many applications [15, 16].

Fig. 5: DLR HOTREG test facility for regenerator and packed bed storage types with pressurized air up 800°C and 10 bar.

Sensible heat storage in liquids

Research and development focuses on the two TES media molten salt and thermal oil in the high-temperature range. There are several material related aspects [17]:

- Identification of new fluids to extend operation temperature window, to enhance the thermal properties (e.g. addition of nano-particles) or lower costs
- Qualification of new fluids in terms of their thermal properties
- The compatibility of fluids with inexpensive filler materials
- The physio-chemical behavior of the fluid in particular near the decomposition temperature
- Metallic corrosion with the TES liquids

The research of storage components aims to replace the two tanks by a single tank with stratification over the height. There are three defined zones in the tank: cold zone (at the bottom), mixing zone (in between), and hot zone (at the top). Some systems operate without filler material (thermocline concept) and some systems utilize additional filler materials within the liquid volume (thermocline-filler concept). This filler can improve stratification and minimize effects from free convection and conduction which can destroy the thermocline zone. In addition overall capital costs can be reduced by the replacement of an expensive liquid with an inexpensive filler material.

Mineral oil can be used at ambient pressures up to about 300 °C. Synthetic oils are thermally stable up to 400 °C, but at higher temperatures they have to be pressurized which is often uneconomic. The flammability and the price of mineral oil are disadvantages of oil systems. Potentially an inexpensive filler material, such as cast iron or natural stone, could storage thermal energy and replace some thermal oil volume. Applications considered are conventional and solar thermal power plants [5, 18].

As the commercial two-tank molten salt concept, the molten salt thermocline with and without filler could operate in a range from 170 to 560 °C depending on the salt mixture. As filler typically natural rock is considered a suitable candidate. There are several research aspects in the areas of heat and mass transfer, thermomechanics, material compatibility, operational aspects, scaling issues and system integration (Fig. 6). If these challenges can be overcome, there is a high potential of cost reduction of the thermocline-filler concept of up to about 40 % compared to the commercial two tank concept [19].

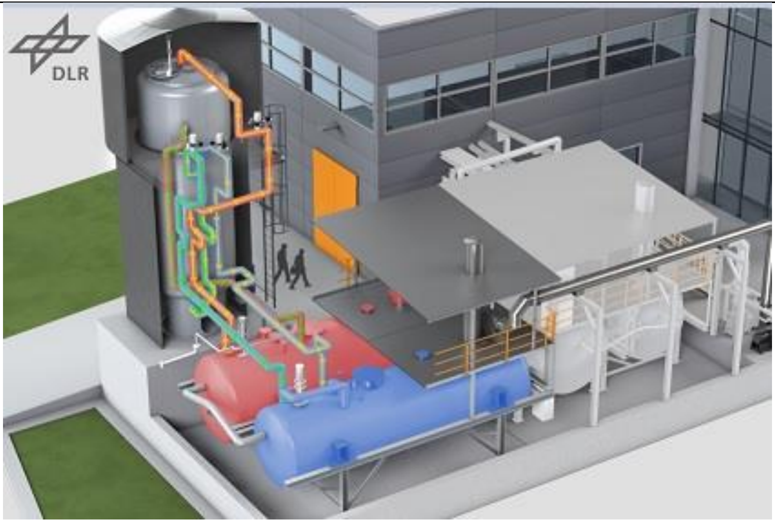

Fig. 6: DLR test facility for thermal energy storage in molten salt (TESIS) – TESIS:store - storage test section for thermocline-filler one tank concept.

Latent heat storage with phase change materials

Latent heat storages generally use a reversible solid-liquid phase change to store large amounts of energy. Materials for the storage of latent heat are called phase change materials (PCMs) because they change their physical phase from solid to liquid and vice versa. Cold storage is deployed in the well-known ice-water phase change (previously as cold stores and currently as modern ice storages). This principle can be applied to temperatures above 150 °C and doing so uses the solidification and enthalpy of fusion of nitrite and nitrate salts. Potential applications emerge in the storage of steam in a temperature range from 150 °C to 350 °C for steam backup systems, industrial process steam and solar thermal power stations with direct steam generation.

One critical challenge is the low thermal conductivity of the salt. Hence, enhancement of the heat transfer is important. For example a concept with aluminum finned tubes embedded in the salt has been developed (Fig. 7). During the charging process, the steam condenses inside the pipes and the PCM melts. During discharging, the solidifying PCM releases heat, the water evaporates inside the pipes, and steam is generated. High temperature latent heat storage systems have already been tested as prototypes coupled to pressurized water/steam cycles (Fig. 7).

In order to supply a more constant power during charging and discharging new active storage concepts are being developed. These concepts aim for an intermediate fluid or transportation of solid PCM along the heat exchanger surface to improve the technology further [3].

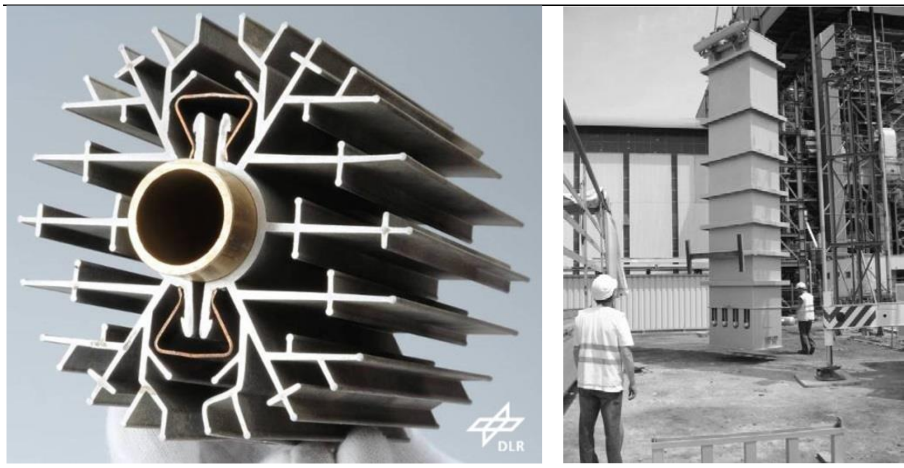

Fig. 7: Photos of steam/water containing steel tube with aluminum fins to enhance heat transfer (left, figure without PCM in between the fins) and DLR prototype PCM-storage module (right, figure shows storage module without insulation).

Thermochemical storage

Thermochemical storage (TCS) systems are currently in a research and development stage. Yet they offer specific potential advantages compared to other TES technologies. These include the long-term storage at room temperature, high energy density, possibility to upgrade thermal energy, switchable heat release and powder transportation capability. These unique features can lead to the opening up of new TES markets.

Three operating conditions are relevant for a thermo-chemical storage unit:
1. Charging - with the use of a heat supply to dissociate an educt, typically a solid material, into a second solid and gaseous product
2. Storage
3. and discharging – respectively, the recovery of heat during the back reaction that emerges in the original solid.

The principle can be repeated over many cycles and may also be deployed in a wide temperature range from below 0 °C to over 1000 °C. The two major TCS classes are sorption (absorption and adsorption) and solid-gas reactions. Depending on the temperature level, different chemical pairs can be used. Examples of solid-gas reactions are hydride/hydrogen, salt hydrate/steam, salt hydroxide/steam and metal oxide/oxygen with several other potential candidates.

One example for high-temperature thermochemical storages is based on the reversible reaction of quick lime and water. This research is motivated by the high energy density in combination with very low material costs and the possibility for long-term storage solutions. Current research focusses on the storage reactor design with temperatures from 400 °C to 600 °C, the movement of bulk material and the system integration with water (or steam) as its reaction partner (Fig. 8) [20].

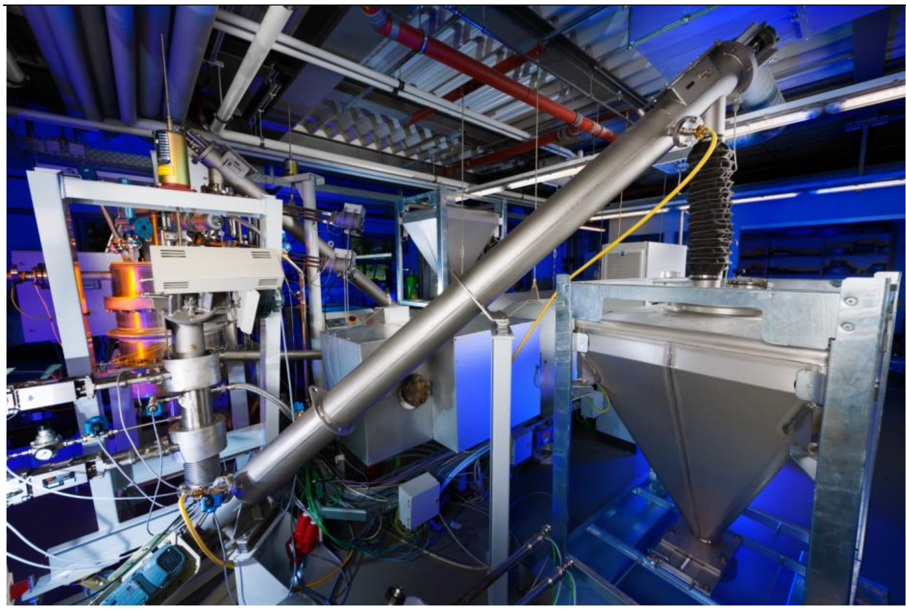

Fig. 8: DLR TCS-test facility for thermochemical storage based on quick lime and water.

Summary and conclusion

High-temperature thermal energy storage (TES) is a vital technology to improve the energy efficiency and to make fluctuating renewable energy controllable and dispatchable. With a changing electricity market and coupling of the electricity and heat sectors, the power-to-heat technology gains importance. However, simple coupling of fluctuating renewable electricity from wind and PV to a rather constant industrial process heat demand via power-to-heat technology is often not feasible. Power-to-heat in combination with high-temperature TES technologies is one option to overcome the challenge of this temporal mismatch and this option allows for the integration of a large share of volatile renewable electricity.

High-temperature TES is a cross-sectional technology which is utilized not only in the industrial process heat sector but also in other application fields such as conventional and solar thermal power plants. Due to the diverse applications of high-temperature TES, there is a potential for technology transfer from other fields to the industrial process heat sector. For example, molten salt storage became recently fully commercial in large-scale solar thermal power plants. Hence, recent high-temperature TES developments can be transferred to the industrial process heat sector.

Not only the transfer of commercial TES technologies, but also new TES approaches in a R&D stage result in possibilities to improve the energy efficiency in the process industry. As discussed in this article, there are several advanced TES technologies being further developed. These technologies have advantages such as reduced investment costs, simpler system integration, higher energy densities or improved adaption to specific heat transfer fluids or temperature levels.

Utilization of high-temperature TES is feasible for different tasks and applications in the process heat sector. They include the fields of batch processes, balancing of discontinuous heat demand or supply, combined heat transport and storage, reduction of part load, reduction of start-up/shut-down losses, supply of backup power and the transition to flexible combined heat and power operation. Overall existing and new high-temperature TES technologies offer several opportunities to meet the diverse demand of the process industry.

Literature

[1] Nägler, T., Simon, S. et al. (2016) Potenziale für erneuerbare Energien in der industriellen Wärmeerzeugung, BWK 68(6): 20-24

[2] Ausfelder, F., Beilmann, C. et al. (2015) Energiespeicherung als Element einer sicheren Energieversorgung, Chem. Ing. Tech. 87(1-2): 17-89.

[3] Bauer, T., Steinmann, W.-D. et al. (2012) Chapter 5: Thermal energy storage materials and systems, Annual Review of Heat Transfer, Vol. 15. G. Chen, Begell House, Inc.: 131-177.

[4] Laing, D., Zunft, S. (2014) Using concrete and other solid storage media in thermal energy storage (TES) systems. In: Advances in Thermal Energy Storage Systems - Methods and Applications. Woodhead Publishing Series in Energy, Woodhead, ISBN 9781782420880: 65-86.

[5] Beckmann, G., Gilli, P.V. (1984) Thermal Energy Storage: Basics, Design, Applications to Power Generation and Heat Supply, Springer.

[6] Steinmann, W.D., Eck, M. (2006) Buffer storage for direct steam generation, Solar Energy, 80: 1277–1282.

[7] Stahl, K., Zunft, S. (2012) Entwicklung eines Hochtemperatur-Wärmespeichers zur Flexibilisierung von GuD-Kraftwerken. In: Kraftwerkstechnik, Bd. 4, TK Verlag. 44. Kraftwerkstechnisches Kolloquium 2012, Oct. 2012, Dresden, Deutschland. ISBN 978 3 935317 87 0: 777-784.

[8] Zunft, S., Dreißigacker, V., Krüger, M. (2014) Einsatz von Hochtemperaturspeichern in der Kraftwerkstechnik und ihre Entwurfsaspekte. In: Kraftwerkstechnik 2014 - Strategien, Anlagentechnik und Betrieb, Saxonia. 46. Kraftwerkstechnisches Kolloquium, 14.-15. Oct. 2014, Dresden. ISBN 978-3-934409-62-0: 637-646.

[9] Krüger, M., Dreißigacker, V., Zunft, S., Meier, H.-J. (2015) Flexibilisierung von Kohlekraftwerken durch Integration von Wärmespeichern: Ergebnisse des Verbundvorhabens Partner-Dampfkraftwerk. In: Kraftwerkstechnik 2015: Strategien, Anlagentechnik und Betrieb. SAXONIA. Kraftwerkstechnisches Kolloquium, Dresden.

[10] Zunft, S., Krüger, M., Dreißigacker, V., Mayer, P.–M., Niklasch, C., Bertsch, C. (2012) Adiabate Druckluftspeicher für die Elektrizitätsversorgung – der ADELE-Wärmespeicher, In Kraftwerkstechnik, Vol. 4. Dresden: TK Verlag: 749–757.

[11] Zunft, S., Hänel, M., Krüger, M., Dreißigacker, V. (2014) A design study for regenerator-type heat storage in solar tower plants – Results and conclusions of the HOTSPOT project. Energy Procedia 49: 1088 – 1096.

[12] Dreißigacker, V. Müller-Steinhagen, H., Zunft, S. (2010) Thermo-mechanical analysis of packed beds for large-scale storage of high temperature heat, Heat Mass Transfer, 46: 1199–1207.

[13] Laing, D., Bahl, C., Bauer, T., Fiß, M., Breidenbach, N., Hempel, M. (2011) High temperature solid media thermal energy storage for solar thermal power plants, in Proc. IEEE Special Issue Paper: 1–9.

[14] Hoivik, N. (2016) Demonstration of EnergyNest Thermal Energy Storage (TES) Technology, SolarPaces Conference, Abu Dhabi 10-14. Oct. 2016.

[15] Odenthal, C., Steinmann, W.D., Eck, M. (2015) The CellFlux Storage Concept for Increased Flexibility in Sensible Heat Storage, Energy Procedia, 73: 244-253.

[16] Schlipf, D., Schicktanz, P., Maier, H., Schneider, G. (2015) Using Sand and other Small Grained Materials as Heat Storage Medium in a Packed Bed HTTESS, Energy Procedia, 69:1029-1038.

[17]Bauer, T., Pfleger, N., Laing, D. et al. (2013) Chapter 20: High temperature molten salts for solar power application, in "Molten Salt Chemistry: from Lab to Applications, " edited by Lantelme, F. and Groult, H., Elsevier.

[18] Bruch, A., Fourmigue, J.F., Couturier, R., Molina, S. (2014) Experimental and Numerical

Investigation of Stability of Packed Bed Thermal Energy Storage for CSP Power Plant, Energy Procedia, 49: 743 -751.

[19] Odenthal, C., Breidenbach, N., Bauer, T. (2016) Modelling and operation strategies of DLR's large scale thermocline test facility (TESIS), SolarPaces, Abu-Dhabi 11.-14. Oct. 2016.

[20] Schmidt, M., Gollsch, M., Grün, M., Giger, F. , Linder, M. (2015) Development of a Moving Bed Pilot Plant for Thermochemical Energy Storage with CaO/ Ca(OH)2, SolarPaces, Cape Town, South Africa, 13 - 16 Oct. 2015.