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Sorption based long-term thermal energy storage – Process classification and analysis of performance limitations: A Review

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Abstract

In sorption heat storage, one of the sources of discrepancy between theoretical material based energy storage potential and resulting system performance is the choice of process type. In this paper, in order to understand this performance deviation, a sorption heat storage process categorisation is proposed. This is followed by a review of reported sorption systems categorised according to the proposed process classification. An analysis of the reported systems is then undertaken focusing on the ratio of resulting temperature gain in sorption (ad- or absorption) compared to required temperature lift in desorption. This measure is termed temperature effectiveness and enables a form of system performance evaluation in the broad landscape of sorption thermal energy storage demonstrators. It is argued that other performance parameters such as volumetric energy storage density and volumetric charge and discharge power density are not adequate for comparison due to the highly varying testing conditions applied. From the system evaluation, it is seen that best temperature effectiveness is generally found in a closed, transported process with the ability of single sorbent pass and true counter flow heat exchange.

Highlights

- There are four basic sorption thermal energy storage processes, open fixed, open transported, closed fixed and closed transported.
- Temperature effectiveness, the ratio of resulting sorption temperature lift to required desorption temperature lift, is a universal means for sorption heat storage system performance comparison.
- Closed transported sorption thermal energy storage systems show the best performance in respect to temperature effectiveness.

Keywords

- Long-term sorption thermal energy storage
- Temperature effectiveness
- Process categorisation
- System performance evaluation
- Comparison across basic designs
- Evaluation of design dependent performance degradation

Word Count

7307 words, excluding title, author names and affiliations, keywords, abbreviations, table/figure captions, acknowledgments and references.

List of abbreviations

GTL_S: Gross temperature lift resulting in sorption (adsorption or absorption)

GTL_D: Gross temperature lift required in desorption

HTF: Heat transport fluid

HMX: Heat and mass exchanger

TE: Temperature effectiveness, GTL_S/GTL_D

WBT: Wet bulb temperature

1 Introduction

Thermal energy storage is an important enabler for the utilisation of renewable energy as well as waste energy. It is applied on a time scale from hours and days up to several months, in the latter case referred to as long-term or seasonal thermal energy storage [1, 2]. This is an important asset for renewable heating of buildings [3-7]. Research activities in the field of long-term thermal energy storage have increased and a broad range of system designs employing different storage materials has been evaluated and tested. Principal criteria for long-term thermal energy storage are among others, high energy density, low thermal loss during storage time and low investment cost. The last mentioned is a critical factor, due to the low number of cycles and thus low overall energy turnover leading to high energy capacity cost (EUR/kWh) [8]. The discipline of long-term thermal energy storage is divided into sensible, latent, and sorption thermal energy storage involving adsorption, liquid absorption and solid absorption with hydration and hydroxide reaction. In this study all processes will be referred to as sorption. Both sensible and latent storage systems suffer continuous heat loss, a substantial challenge for long-term storage applications, countered by large scale sensible storage systems [9] and supercooling in latent systems [10, 11].

Sorption thermal energy storage follows the concept of reversible decomposition reaction process [12-19]. In the action of sorption, sorbate in its gaseous phase is adhered to or penetrates into a solid or liquid sorbent [13, 14, 20]. A combination of thermophysical and thermochemical processes are involved [21, 22]. This approach has the prospect for high energy density and lossless storage over time making it attractive for long-term heat storage [14, 23, 24]. Not actually heat but the potential to regain heat at a later point in time and at elevated temperature is stored, functioning as a chemically driven heat pump accessing heat from a low temperature source. Temperature swing is usually followed in the process [13] involving a temperature difference defined and referred to as gross temperature lift (GTL). In desorption, heat is employed, effecting a GTL_D in order to remove sorbate, typically water from the sorbent through evaporation, reaching an increase in sorbent mass fraction and establishing a potential for sorption. In the sorption process on the other hand, sorbate is evaporated and adheres to or penetrates into the sorbent whereby the sorbent mass fraction declines and sorbate heat of condensation as well as heat of reaction is released reaching a material and mass fraction specific GTL_S.

Some criteria for choice of sorption materials stated in literature are [20, 23, 25, 26]:

- Desorption and sorption temperatures fitting to specific application
- High affinity of sorbent to sorbate – (affecting both GTL as well as volumetric charge and discharge power)
- High specific volumetric uptake of sorbate on sorbent – (affecting volumetric energy storage density)
- Substantially higher volatility of sorbate than sorbent – (for good separation through evaporation)

- Good mass and heat transfer characteristics – (affecting charge and discharge power)
- Good chemical and mechanical stability – (affecting cycle stability)
- Favourable life cycle properties such as ecology and embodied emissions – (positively affecting sustainability)
- Low material price – (affecting economic viability)

Other criteria considered are corrosiveness, toxicity and moderate operation pressure. Nevertheless, these issues are disputable and appropriate coating and system engineering solutions may be found to mitigate potential negative impact performance, longevity or acceptance.

In the present work, contrary to many other review papers on long-term sorption thermal energy storage systems, a critical reflection on performance and comparison of various systems published in literature is made. There are four basic measures of performance that can be applied. These are: GTL, volumetric energy storage density, volumetric charge and discharge power density, and charge to discharge round trip efficiency [20, 23, 25, 26]. Previous review papers [18, 27-31] have followed the practice of citing power and energy density of various technologies and proof of concept systems as reported. This can be misleading, due to the substantial dependency of both volumetric energy storage density and volumetric charge and discharge power density on operating temperatures. Even if operating temperatures are specified, due to the non-uniform testing parameters direct comparison cannot be made. Energy density and power density comparison between different systems is only possible if system tests are performed at defined application specific operating temperatures and if clear definition of referred volume in respect to material or system is reported [32]. For this reason, in this paper a system evaluation based on the reported ratio of resulting GTL_S in sorption in respect to the required GTL_D in desorption defined as temperature effectiveness (TE) is resorted to. GTL is a measure that can be applied along the scale from material to component and system, as a means of analysis of performance reduction along the scales, and is applicable for all sorption materials [32]. In this work the ratio of GTL_S to GTL_D referred to as TE is employed as a method to describe how well the system takes advantage of the full potential of the employed storage material. This enables a comparison between the systems as well as the basic processes used. Even though operation dependencies remain in this evaluation, this approach is substantially more robust since dependency is reduced to the sorbate vapour pressure. In as far as the vapour pressure remains constant both in desorption and sorption, theoretical temperature effectiveness is unity. Figure 1 shows different isosteres for aqueous NaOH (left) and zeolite (right) illustrating vapour pressure dependency of the GTL. In the diagrams the theoretical GTL at 1 kPa is compared to the GTL at 10 kPa vapour pressure. It is clearly shown that at greater sorbent vapour pressure the GTL increases. This is noted by the red circled line.

Figure 1: Isosteres of aqueous NaOH [33] on the left side and zeolite [34] on the right side, at varying sorbate mass fractions. Indicated is the difference between GTL evaluated at a vapour pressure of 1 kPa and 10 kPa respectively.

In the application as long-term thermal storage, it is expected that the vapour pressure in desorption is typically greater than the respective pressure in sorption. Thus results that GTL_s is smaller than GTL_D and TE is less than unity. In the case where non-realistic vapour pressure conditions are followed, in a sense that higher pressure is taken in sorption than in desorption this leads to a more favourable TE evaluation.

TE as a measure of comparison between sorption systems thus benefits from non-confinement to a specific material, system approach or testing procedure. Since GTL is a temperature difference, specific operating temperatures apart from the discussed vapour pressure are eliminated from the comparison and no reference to volume is required. These are both important criteria since no specific uniform testing procedure is followed in the reported experiments. In the comparison, high TE shows good temperature management performance, pointing to a reduced process based temperature drop both in sorption as well as desorption. For the analysis presented herein care is taken to resort to heat transport fluid (HTF) temperatures and not storage material temperatures as well as average temperatures where relevant in dynamic discharging processes. In addition, comments are made on unrealistic testing conditions in light of the application as domestic heat storage. Pictures of the systems used for comparison are provided to give the reader an understanding of how far these prototypes are from real application.

2 Sorption thermal energy storage system processes

Systems focussed on in research and reported in literature can be classified into the process variations open versus closed [23] and fixed versus transported [13]. The former refers to material contact to the ambient air and the latter deals with sorbent material handling. A similar process classification is found proposed by [35] whereby reference is made to open, closed and liquid.

According to [36], some long-term thermal energy storage system challenges are:

- Choice of the best process (open or closed)
- Heat and mass exchanger (HMX) design and the reactor configuration
- Pressure drop
- Efficiency
- Cost

To date, choice of process, HMX design as well as therefrom resulting system design is largely based on choice of sorbent material. Sorbents that react with CO_2 , are hazardous or easily airborne, are studied in closed systems [37], and non-hazardous mainly solid materials are often employed in open systems for reason of their simplicity [38]. Solid sorbents are primarily studied in fixed systems with some work done on agitated transported processes [39] and transported sorbent systems are largely used for liquids [37, 40]. Figure 2 illustrates the four basic sorption heat storage processes, separating open and closed on the x-access and fixed and transported on the y-access. Illustrations are numbered for further reference.

Figure 2: Illustration of basic sorption thermal energy storage processes.

2.1 Open process

The open process (illustration 1 and 3 in figure 2) operates solely with water as sorbate at atmospheric pressure. Sorbate is released to and sourced from the atmosphere [41]. This is illustrated by the pump symbol sourcing sorbate from the ambient. Systems based on the open process consist of a sorption and desorption HMX and a sorbent storage unit [13]. These systems do not have an evaporator and condenser unit or sorbate storage [42] and do not require vacuum or pressure compliance [41]. Thus, respective system complexity and volume are reduced. Discharge power directly depends on the given partial vapour pressure of sorbate in the ambient air [43]. This is generally low due to the low ambient temperature during the heating season. For this reason high volumetric air flow is required to reach adequate humidity supply [44]. This corresponds to a large thermal mass of inert carrier gas flow, limiting effective GTL_s, discharge power and discharge efficiency through effected cooling [13]. In order to improve performance, air to air heat exchangers for heat recovery [39] and air humidifiers are employed [44], leading to an increase in complexity, system volume and cost. To increase vapour mass transport in the supply air, water is sprayed into the air stream bringing about an air temperature reduction at increased relative humidity. A general challenge in the open process is fouling on the sorbent material by heavy contaminations, bringing about a decline in temperature gain and power losses over time [20].

2.2 Closed process

In the closed process (illustration 2 and 4 in figure 2) the sorbate and sorbent is not in direct contact with the atmosphere and the sorbate is stored separately [13]. Thus, the open process exchanges matter while the closed process exchanges only heat with its surroundings. Closed systems consist of a sorption and desorption part as well as an evaporator and condenser part of the HMX, and sorbent and sorbate storage vessels [45]. They operate under sorbate atmosphere generally below atmospheric pressure, require good sealing [13] and are highly sensitive to the presence of non-condensing gases [40, 46]. Closed systems reject heat to and source it from the

ambient, typically the ground or the air [13] and are not bound to water as sorbate. Even so, water is often used due to its high phase change enthalpy from liquid to gas as well as generally high solubility in, and high affinity to, the respective sorbents [16]. Sorbent and sorbate are stored in separated vessels and the sensible part of the thermal energy employed for material separation is released to the atmosphere [13]. In sorption, the system output temperature is dependent on the low temperature heat source supplied to the evaporator and the sorbent material based GTL. In liquid sorbents GTL is dependent on sorbent mass fraction, whereby in solids it is dependent on the level of hydration.

In order to simplify comparison of closed and open systems in respect to vapour pressure and temperature gain, it is favourable to convert a given partial water vapour pressure in air to its wet bulb temperature (WBT). This corresponds to the respective evaporation temperature in a closed system. Since the WBT is always lower or equal to the ambient temperature, sink and source temperature is greater for closed systems than open systems. Thus, closed systems potentially require higher desorption temperatures but also release higher output temperatures than open systems [47]. This is most critical in the heat release in sorption, where it is important to reach high output temperature and maximum state of discharge. In this respect, closed systems are superior for the task of heating in buildings.

2.3 Fixed process

In the fixed bed process (illustration 1 and 2 in figure 2) the sorbent is kept stationary and often combined with the heat and mass exchanger [48]. No separate storage vessels are required [29], but an interdependence of desorption and sorption power and storage capacity results [13]. This is the most frequently followed process approach with solid sorbents [29, 43]. In the design of a fixed bed system it is important to know how sorption and desorption transitions progress through the bed [20, 49]. This introduces the factors time and space into the analysis, leading to a dynamic character. Practical aspects such as mass transport, thermal conduction, dispersion phenomena at bed scale and volume change are important parameters to be considered [20]. Fixed bed systems generally suffer high pressure drop through the bed, reducing potential GTL_s and requiring high parasitic power consumption [50]. In the desorption process, the complete sorbent bed is heated and has to be maintained at a material specific desorption temperature in order to reach the desired charged state [51]. In sorption the same process is followed, whereby through sorption based heat release, the complete bed is heated to the sorption temperature [49, 52]. It follows that high thermal capacity of the material leads to system capacity loss. The sorption process is maintained until the output temperature drops below the minimum required output temperature, referred to as thermal breakthrough. The achievable storage density decreases drastically, when the thermal breakthrough temperature is increased [47]. In non-continuous sorption, sorbate mass transfer during inactive periods may occur and lead to the establishment of a new homogeneous state of charge at a lower potential GTL_s and thus lower maximum output temperature in continued discharge [41]. Segmentation of storage vessels is employed in order to reduce issues with partial discharge [41], as well as enable discharge below breakthrough threshold through connection of segments in series [53]. Complexity in fixed bed application is increased when used for heat storage purposes through heat recovery, compared to other fixed bed striping processes. In the design of heat exchangers two approaches are followed, integrated including direct air heating [42, 44, 54] and separated [13]. Integrated heat exchangers are placed inside the fixed bed, while separated heat exchangers are positioned separate from the sorbent downstream from the sorbent supply. In both approaches, a mean temperature results. This temperature is substantially lower than the maximum temperature that can be reached based on the mass fraction specific GTL_s.

2.4 Transported process

In the transported process (illustration 3 and 4 in figure 2) the heat and mass exchanger unit is separated from the sorbent storage [18]. Thus, separate storage vessels and means of sorbent transportation are required [29, 45]. In this approach, heating power and thermal energy capacity are separated and can be individually designed and scaled for a specific application [13]. Due to

the sorbent transport and continuous supply of fresh sorbent a steady state operation can be reached in the HMX [20], leading to continuous desorption or sorption with steady temperature and power profiles. This is in strong contrast to the fixed approach with dynamic profiles in the sorbent bed. Reaction processes are thus reduced to a fraction of the total storage material [55]. Sorbent transport parameters, such as viscosity and wetting behaviour for liquids [56] and grain size, material stability and flowability for solids [49] are important. Liquids are beneficial due to their simple transport by pumping [18, 45]. For solids three basic reactor types are discussed, fluidised bed, extruder reactor and bulk flow reactor [49, 51]. In the design of the heat and mass exchanger two characteristics are of significant benefit: sorbent single pass and counter flow. Recirculation of partly discharged sorbent, as typically employed in liquid sorbent chillers for good wetting, will lead to substantial reduction of the maximum discharge temperature due to mixing of fresh and partly discharged sorbent. Counterflow of sorbent and HTF is important for optimal heat exchange from sorbent to HTF. In this way maximum output temperature is reached due to continuous contact of HTF to fully charged sorbent and maximum discharge is enabled through cooling of sorbent to minimum heat transfer fluid temperature.

Considerations of best HMX design in terms of sorbent velocity, vessel height, contact area of sorbent to sorbate and heat transfer fluid, exposure time and sorbent flow distribution is important for optimum sorption kinetics both for liquid and solid sorbents. Due to the single pass requirement, slow flow with good liquid wetting or solid contact for improved thermal conductivity and high sorption surface area is key [45]. Residence time and hence, the HMX holdup is an important design feature in order to enable close fit to temperature and vapour pressure equilibrium for maximum storage capacity. It follows, that for heat storage, a heat and mass exchanger is designed on the basis of sufficient sorbent holdup or exposure time rather than on the basis of high mass transfer rate for maximum power density.

In comparing fixed systems to transported systems it can be concluded that, in as far as single pass and counter flow is followed, transported systems are superior both in low GTL_D and high respective GTL_S as well as in capacity [49]. Fixed systems are discharged to the HTF output temperature and maximum GTL_S is not reached due to bulk thermal capacity and internal mixing of heat from sorbent at varying mass fraction. Transported systems on the other hand are discharged to the heat transport input temperature, which is naturally lower than the output temperature [41]. Thus, fixed systems are sensitive in capacity to the output temperature [47] while transported systems are not [57] in as far as they reach the required temperature. For both fixed and transported systems capacity decreases if the HTF input temperature increases in respect to the sorbate evaporation temperature. Table 1 gives an overview of the process advantages and disadvantages.

Table 1: Advantages and disadvantages of the basic sorption thermal energy storage process types.

Process	Comment	Advantages	Disadvantages
Open fixed	<ul style="list-style-type: none"> - limited to water as sorbate - may require air to air heat exchanger and air humidifier - power and capacity are interlinked 	<ul style="list-style-type: none"> - operation at atmospheric pressure - only 1 HMX needed - no sorbate storage needed - no sorbent transport required - possibility to use process air for heat exchange 	<ul style="list-style-type: none"> - low vapour pressure in ambient air - requires high volumetric air flow - issues with fouling of sorbent - only for non-hazardous sorbents - dynamic process parameters temperature and power - batch wise desorption and sorption and capacity loss under discontinuous operation - high parasitic heat capacity - high pressure drop for air based heat exchange - reduced GTL_s - maximum discharge to output temperature
Open transported	<ul style="list-style-type: none"> - limited to water as sorbate - may requires air to air heat exchanger and air humidifier - separate scaling of power and capacity 	<ul style="list-style-type: none"> - operation at atmospheric pressure - only 1 HMX needed - no sorbate storage needed - steady state process - continuous desorption and sorption - capable of single pass and counter flow - maximum GTL_s - discharge to minimum input temperature - possibility to use process air for heat exchange 	<ul style="list-style-type: none"> - low vapour pressure in ambient air - requires high volumetric air flow - issues with fouling of sorbent - only for non-hazardous sorbents - Increase in complexity, storage vessels and means of transport

Closed fixed	<ul style="list-style-type: none"> - applicable to non-water sorbates - power and capacity are interlinked 	<ul style="list-style-type: none"> - increased vapour pressure and density - no fouling of sorbent - no sorbent transport required 	<ul style="list-style-type: none"> - operates at sub atmospheric pressure - requires condenser and evaporator - sensitive to non-condensing gases - requires sorbate storage - dynamic process parameters temperature and power - batch wise desorption and sorption - high parasitic heat capacity - high pressure drop for air based heat exchange - reduced GTL_s - max discharge to output temperature - low heat transfer between sorbent and HX with solids
Closed transported	<ul style="list-style-type: none"> - applicable to non-water sorbates - separate scaling of power and capacity 	<ul style="list-style-type: none"> - increased vapour pressure and density - no external fouling - steady state process - continuous desorption and sorption - capable of single pass and counter flow - maximum GTL_s - discharge to minimum input temperature 	<ul style="list-style-type: none"> - operates at sub atmospheric pressure - requires condenser and evaporator - sensitive to non-condensing gases - requires sorbate storage - Increase in complexity, storage vessels and means of transport - low heat transfer between sorbent and HX with solids

3 Examples of systems from literature

In the following section, examples of systems reported in scientific literature of all four basic sorption processes are taken and compared based on temperature effectiveness (TE). The comparison does not include reference to power or energy density for reasons specified in the introduction.

3.1 Open fixed

There are many institutes working on open systems with fixed bed reactors. Segmented vessels with shallow beds for reduced pressure drop, improved thermal response and reduced release of heat to bulk sorbent due to material thermal capacity are looked into [44, 58-60]. In general, air

serves as both heat and sorbate transport medium and building integration via forced air ventilation is focused on. This is due to the potentially higher vapour pressure in the air released from buildings. Nevertheless, this approach does not introduce external heat to the building but only more thoroughly recovers heat from the building. In the following examples, remarks on claimed volumetric energy storage density and volumetric charge and discharge power density are provided in the discussion, but are not the focus of comparison.

At the University of Lyon, France, in collaboration with the University of Savoie, France, an open fixed bed system has been designed consisting of two drum-like containers, in a segmented fixed bed storage design. The sorbents zeolite Na-X [58] and zeolite 13X [45] are tested in the setup. The applied desorption temperature is 180 °C. This is a challenging temperature to reach apart from electric resistive heating and represents a difficulty in all zeolite based systems. The ambient temperature and relative humidity in turn are not specified in the respective reporting. If 25 °C and 55 % RH is taken as average temperature and humidity values for Lyon, equalling to a WBT of 15 °C, the GTL_D is 165 K. Sorption is performed at an air temperature of 20 °C and 70 % RH, equal to a WBT of 14 °C. This is a high WBT even for air recovery in buildings, considering that the sorption process takes place in the cold season when the indoor relative humidity is typically low in the range of 30-50%. The reported output temperature is approximately 57 °C as shown in figure 3 right, resulting in a GTL_S of 43 K.

Figure 3: Left: Prototype open fixed bed system with dual storage compartments operated with zeolite Na-X and zeolite 13X. Right: Output temperature vs. time curve of a sorption test with zeolite Na-X from the University of Lyon, France [58].

A material specific volumetric energy density of approximately 85 kWh/m³ is reported, noting that a reduction in desorption temperature to 120 °C and thus 105 K GTL_D leads to a decline in energy density to 60 kWh/m³. This points out the substantial effect that charging GTL_D has on storage density. Further substantial decline in both energy density and kinetics would have to be accounted for if the WBT is adapted to more realistic operation conditions. Due to the shallow bed design, a steep temperature drop is encountered at breakthrough temperature. The sorbent cannot be discharged beyond this temperature threshold. With zeolite 13X at identical desorption and sorption conditions as followed for zeolite Na-X, GTL_S was 44 K and at 20 °C but lower WBT of 9 °C, GTL_S of 37 K was reached. This shows that GTL_S is affected by the WBT.

A tray type segmented fixed bed reactor was reported by Michel et al. from PROMES-CNRS, France [61], based on the solid sorption salt pair SrBr₂ and water. Segmentation is followed in order to reduce pressure drop. Shallow beds are designed and operated in parallel. The applied GTL_D in desorption is approximately 62 K with a desorption temperature of 82 °C and a WBT of 20 °C. These desorption settings are more realistic for a direct solar heated or heat pump assisted desorption process. The resulting GTL_S is 19 K with an output temperature of approximately 25 °C and a WBT of 6 °C. In figure 4 bottom, the operation conditions are displayed in a Clausius–Clapeyron diagram.

Figure 4: Top Left: Illustration of the reactor prototype including dimensions and air flow path. Top right: Picture of the installed trays. Bottom: Experimental operating conditions for the reactor prototype based on the $\text{SrBr}_2 \cdot 1-6\text{H}_2\text{O}$ reaction, in a Clausius–Clapeyron diagram [61].

In the frame of the SolSpaces project an open fixed bed sorption storage system was developed at ITW Stuttgart, Germany [42]. The employed working pair is zeolite 13XBF and water. Desorption temperature is reported to be 180°C at 10 mbar partial water vapour pressure equal to a WBT of 8°C , thus a GTL_D of 172 K is applied. In sorption, air is supplied at approximately 26°C and relative humidity of 38 % equal to a WBT of 10°C . The resulting GTL_S is approximately 42 K if an average output temperature of 52°C is taken, as visible in the temperature profile in figure 5 bottom right. This is an example where the thermal testing conditions are substantially out of the domestic heat storage application scope, especially since the WBT in desorption is lower than in sorption.

Figure 5: Top: Pictures of the system in construction. Bottom left: Vertical cut through the vessel with air flow indication. Bottom right: Temperature profile in sorption of the SolSpaces project demonstrator. [42].

At Shanghai Jiao Tong University, China, work is performed on a segmented packed bed storage, operating on the solid sorption composite material activated alumina and lithium chloride [62]. Contrary to the previous described setups, storage segments are installed vertically and in series. Desorption temperature is 110 °C whereby the GTL_D is not clear, since no partial vapour pressure is indicated. Under the assumption of 25 °C and 55 % RH, equal to a WBT of 15 °C, GTL_D is 95 K. Sorption is performed at an air temperature of 20 °C and relative humidity of 60 % RH, 70 % RH and 80 % RH with WBT 12 °C, 14.4 °C and 16.5 °C respectively. These values are substantially higher than available for building heating application. In the report, it is noted that maximum discharge temperature depends on the relative humidity, which is clear, since the respective WBT changes, while the GTL_S of 27 K, 27.3 K and 28 K respectively remains relatively constant, as discussed in the introduction. Figure 6 bottom right, shows the sorption results under the varying relative humidity. It is also noted that the energy density of segment 1, approximately 230 kWh/m³, is greater than segment 2, which has approximately 130 kWh/m³. The explanation to this phenomenon can be seen in the temperature profile, whereby the final discharge temperature of segment 1 is lower than that of segment 2. Consequently, segment 1 has a greater vapour uptake due to the lower temperature. Segment 2 is not able to reach the equal state of discharge since thermal breakthrough temperature prohibits further operation. This is a good example of the benefit of serial connection of storage segments for increased storage capacity.

Figure 6: Top: Schematics of the test bench setup with air supply, humidifier and heater, preceding the dual modules connected in series. Bottom left: Picture of the insulated setup. Bottom right: sorption temperature and humidity results in respect to 60 % RH, 70 % RH and 80 % RH at 20 °C supply air temperature of the Shanghai Jiao Tong University demonstrator [62].

At the University of Nottingham, England, an alternative pipe shaped sorbent storage system design is followed and operated with the solid sorbent composite material vermiculite / calcium chloride as well as tested with the sorbent zeolite 13X [63]. The storage system is segmented into three tube-type vessels holding a perforated inner tube with sorbent packed between the inner and the outer tube. Air is supplied to the inner tube where it spreads to the sorbent and is released at the top of the outer tube to be supplied to the building. Desorption is performed at 80 °C with a vapour pressure of 0.18 mbar, equal to a WBT of -40 °C, thus desorption is performed at a GTL_D of 120 K. Sorption is carried out at 20 °C input temperature and 21.6 mbar vapour pressure, resulting in a WBT of 19 °C. The output temperature is approximately 40 °C, as seen in figure 7 right, thus GTL_S is about 21 K. It must be noted that these operating temperatures strongly violate the application scope, with the WBT in desorption substantially lower than in sorption. In the report it is stated that intermittent sorption of the storage does not affect sorption temperature. This may be due to the low air penetration depth coming from the tube type design, leading to a homogeneous discharge. It may be misleading to assume similar behaviour at larger bulk scale.

Figure 7: Top left: Schematics of the testing rig, illustrating both desorption and sorption processes. Top right: Picture of the test setup. Bottom: Mass change and sorption/desorption rates of the testing rig operated with zeolite and SIM-3a in sorption and desorption cycles with operating temperatures indicated [63].

At the Eindhoven University of Technology in collaboration with ECN in the Netherlands, a segmented fixed bed system consisting of four tanks with a volume of 62.5 L each was developed and tested with the working pair zeolite and water [60]. The material is desorbed at a temperature of 190°C whereby relative humidity is not given. Assuming a WBT of 15°C the GTL_D is 175 K. Sorption temperature is 10°C with a relative humidity of 90 % resulting in a WBT of 8°C . Output temperature is 28°C , whereby a GTL_S of 20 K is reached with an average material specific energy density of 198 kWh/m^3 . Figure 8 shows both the system and operation results. An adjustment to application specific conditions in desorption would again result in substantial reduction of energy density.

Figure 8: Left: Picture of the demonstrator setup. Right top: temperature profile in desorption. Right bottom: Temperature profile in absorption [60].

From the presented demonstration systems it can be seen that the open fixed bed approach leads to substantially lower GTL_S in sorption compared to the required GTL_D in desorption. Low temperature output and reduced energy density are the result. This is due to the high turnover of air with low water vapour partial pressure during discharge and the significant thermal capacity of the sorbent. Further GTL_S reduction comes from mixing of heat streams from sorbent at varying state of charge and it is clear that the system capacity is highly dependent on the thermal breakthrough temperature.

3.2 Open transported

At ITW University Stuttgart, Germany in collaboration with several other German Institutes [38, 64-66], research is performed on open transported system concepts using the sorbent zeolite as well as salt impregnated Zeolites. As with the open and fixed systems discussed, this concept bases on the integration into the building forced air ventilation. A double stage sorption process is followed, whereby the cool moist air initially flows through the pre-reactor and then through the main reactor. In this way a two stage type counter flow is reached and discharge to below the output temperature threshold is possible since the pre-reactor is not bound to the output temperature threshold. Greater discharge is thus possible and higher storage capacity is reached. Nevertheless, due to the cross flow approach, GTL_S at different state of charge is still mixed and consequently maximum temperature gain cannot be reached. Desorption is performed at 180 °C and 10 mbar vapour pressure equalling to a WBT of 7°C and GTL_D is 173 K. Sorption is carried out at an air temperature of 28°C and 15 mbar with WBT equal to 13 °C. These operating conditions are again out of scope for the domestic heat storage application and the WBT in sorption is greater than in desorption. The output temperature after the pre- reactor is approximately 40 °C reaching a GTL_S of 27 K and the temperature after the main reactor is 63°C with a GTL_S of 50 K. Notable in this system approach is the steady state process through sorbent transport and thus steady state output temperatures attributed to the transported system approach.

Work on open transported systems is also performed at the University of Mons, Belgium in collaboration with several other European Universities, within the SOTHERCO projects [67, 68]. Varying concepts are considered with either a vertically positioned moving bed with horizontal air flow or a horizontal circular moving bed reactor with vertical air flow. Again, due to the cross flow approach in both concepts, GTL_S at different state of charge is mixed and thus it is expected that

maximum temperature cannot be reached. The open transported system example given shows that greater discharge and higher output GTL_s can be reached with transported systems compared to open and fixed systems.

3.3 Closed fixed

The Netherlands organisation for Applied Scientific Research TNO has designed a zeolite 5A based closed sorption system [69].

Figure 9: Top left: Picture of the sorber / desorber unit. Top right: Picture of the evaporator / condenser unit. Bottom: Operating result in sorption of the TNO designed zeolite 5A based closed sorption system [69].

The setup consists of a sorber / desorber unit with the sorbent adhered to the heat exchanger and an evaporator / condenser unit consisting of several trays for water suspension with underlined tube heat exchanger. The system is desorbed at 103 °C and 20 °C condenser temperature, resulting in a GTL_D of 83K and sorption is performed at 20 °C input heat transfer fluid (HTF) temperature at an evaporator temperature of 15 °C. Maximum HTF output temperature is 53 °C resulting in a maximum GTL_S of 38 K and an average GTL_S of about 30 K. Figure 9 shows results from the sorption process. These testing temperatures are within realistic application conditions.

At AEE Intec, Austria, work is done on the design of a closed fixed bed sorption heat storage system for domestic application [48]. The system consists of a vessel type containment filled with zeolite 13XBF with integrated heat exchanger for optimised heat transport as well as separate heat and mass exchanger serving as condenser and evaporator connected to a vessel for the liquid sorbate storage. Figure 10 shows the schematics as well as the extensive heat exchanger for the sorbent tank. Desorption is performed at 180 °C and 17 °C condensation temperature, consequently resulting in a GTL_D of 163 K. In sorption, the condensation temperature is set to 20 °C and the discharge temperature is 45 °C thus reaching a GTL_S of 25 K. These temperatures are outside of the domestic heating application conditions. A lower condensation temperature than evaporation temperature is generally not realistic.

Figure 10: Top: Schematics of the AEE Intec closed fixed system. Bottom: Picture of the fixed bed integrated heat exchanger [48].

Work is performed on a closed fixed bed sorption heat storage for domestic application at TNO in the Netherlands in the frame of the MERITS project based on sodium sulphide [53]. The demonstrator consists of several storage vessels incorporating heat and mass exchangers with integrated solid sorbent, as well as heat and mass exchangers for evaporation and condensation of sorbate. Figure 11 shows the proposed system schematics. The working pair is the solid sorbent Na_2S and water as sorbate. Required desorption temperature is stated to be 80 °C at a condensing temperature of 20 °C, hence effecting a GTL_D of 60 K. In sorption an output temperature of 65 °C and evaporator temperature of 10 °C is proposed, suggesting a GTL_S of 55 K. Nevertheless, to

date there are no measured results published. It is expected that operational results will deviate substantially due to the mentioned system design limitations.

Figure 11: Schematics of the Merits system [53].

Palomba et al. from the CNR, Messina, Italy, present a system operating with the working pair AQSOA FAM Z02 / water able to supply heat and cold [70]. Figure 12 shows the schematics and operating results. Desorption temperature is 90 °C at 30 °C condensation temperature, a realistic temperature setting, equalling to a GTL_D of 60 K and evaporation temperature is 10 °C with a sorption temperature of 35 °C and GTL_S of 25 K. These temperatures settings are well fitting to the building heating application. The condensation temperature in desorption is 20 K greater than the evaporation temperature in sorption.

Figure 12: Top left: Picture of the University of Messina setup with sorber / desorber at position 1 and condenser / evaporator at position 2. Top right: Schematics of the test setup. Right: Temperature profiles in desorption and sorption [70].

On the same setup as Palomba, shown in figure 12, in collaboration with the Boreskov Institute of Catalysis and the Novosibirsk State University, Russia, work is done on the composite material LiCl / vermiculite [71]. Initial system demonstrator scale tests were also performed at 90 °C desorption and 30 °C condensation, resulting in a GTL_D of 60 K. As shown in figure 13, in desorption, the evaporation temperature is approximately 12.5 °C and the absorption temperature average taken from the initial 6 minutes is 37 °C, thus a GTL_s of 24.5 K is reached. From the time scale it is visible that this is still a small lab setup.

Figure 13: Operating diagram in sorption with LiCl / vermiculite composite. Right: Evaporator temperatures, Left: Absorber temperatures [71].

Zhao et al. report a fixed bed LiCl / expanded graphite and water working system from Shanghai Jiao Tong University, China [72]. The absorber / desorber consists of a large number of trays containing the LiCl, with attached heat exchanger. Figure 14 shows the setup. Desorption is performed at 85 °C with 18 °C condensation temperature, requiring a GTL_D of 67 K. Evaporation is performed at 18 °C, achieving an sorption temperature of 40 °C and granting a GTL_S of 22 K. Figure 14 shows operating results of the demonstrator.

Figure 14: Top: Picture of the setup as well as the sorber / desorber and evaporator / condenser unit. Bottom: Operating results in desorption as well as sorption of the Shanghai Jiao Tong University demonstrator [72].

At the Institute of Refrigeration and Cryogenics, Shanghai Jiao Tong University, China in collaboration with Sir Joseph Swan Centre for Energy Research, UK [73] work is done on a closed fixed system based on the working pair $MnCl_2$ - $CaCl_2$ - NH_3 where the sorbate is NH_3 . Figure 15 shows a picture of the setup, the theoretical p-T diagram and operating results. On a theoretical basis, the GTL_D is 55 K and the GTL_S is 50 K, as shown in the p-T diagram in figure 15. In operation desorption was performed at a 157 °C at a condensation temperature of 21 °C resulting

in a GTL_D of 136 K. Sorption was performed at an Evaporation temperature of 10.6 °C and the average temperature reached was 58 °C thus achieving a GTL_S of 47.4 K. Figure 15 shows the respective operation diagrams.

Figure 15: Top left: Picture of the test setup operating with the working pair $MnCl_2$ - $CaCl_2$ - NH_3 . Top right: p-T diagram with the theoretical operating temperatures and pressures. Bottom: Diagrams of the desorption and sorption process, indicating temperature and pressure, red dotted lines are included for clarification [73].

Closed fixed systems are often employed for dual mode systems, able to supply both heat and cold [74] or operating on other sorbates than water such as NH_3 [75, 76]. Yan et al. also proposes a system with $MnCl_2$ and NH_3 , with GTL_D of 154 K and GTL_S of 35 K [75]. In general, closed fixed systems reach a higher GTL_S due to the lack of air present in the sorbate transport.

3.4 Closed transported

At the research institute Empa in Switzerland, work is done on closed transported liquid sorption with aqueous sodium hydroxide [45]. The system consists of an absorber and desorber

interconnected to a condenser and evaporator forming a HMX unit for sorbate vapour exchange and storage vessels for charged and discharged sorbent figure 16 shows the schematics as well as a picture of the setup. The heat and mass exchanger is designed so that the sorbent is in counter flow to the HTF. In this approach, the sorbent final temperature in sorption is close to the HTF input temperature. In this way maximum sorbate uptake and maximum HTF output temperature is enabled through constant feed of charged sorbent reaching maximum GTL. Counterflow and single pass enable steady state process in both sorption and desorption. Reported desorption temperature is 65 °C at a condensation temperature of 10 °C with a GTL_D of 55 K. In sorption an average GTL_S of 23 K is achieved with 25 °C evaporator temperature and 48 °C absorber temperature. Again, these test settings must be criticised, since the evaporation temperature is greater than the condensation temperature.

Figure 16: Left: Schematics of the closed transported system. Right: Picture of the lab scale setup [45].

At Tsinghua University, China, a closed transported system based on the working pair LiBr and water is reported [78]. Figure 17 shows the setup as well as operating temperatures. In desorption a temperature of 73 °C with a condensing temperature of 18 °C was applied, coherent to a GTL_D of 55 K. In sorption, evaporator temperature was set to 12 °C, reaching an average absorber temperature of 36 °C resulting in a GTL_S of 24 K. In the setup a tube bundle falling film heat and mass exchanger is employed, and from the schematic illustration and the operation results it can be seen that the sorbent solution is circulated in order to reach good wetting. For this reason, steady state operation is not possible and energy density is reduced due to temperature breakthrough limitation.

Figure 17: Top left: Picture of the test setup. Top right: Schematics of the system. Bottom left: Desorption operation result. Bottom right: sorption operation result [78].

At the University of Savoie, France work is performed on the LiBr and water working pair [79]. Desorption of the system was performed at 95 °C and condensation at 20 °C thus a GTL_D of 75 K was applied. It is reported that in sorption no temperature gain was reached. Figure 18 shows the setup as well as the testing result.

Figure 18: Top: Picture of the LiBr and water system. Bottom: Results of two sorption tests [79]

Figure 19: Top left: Picture of the KCOOH and H₂O test setup from the University of Savoie, France. Top right: Schematics of the setup. Bottom left: Results of the desorption test. Bottom right: Results of a sorption test [80].

Further research at the University of Savoie, is conducted based on KCOOH and H₂O working pair [80]. The desorption process is performed at 59 °C at a condensing temperature of 16 °C resulting in a GTL_D of 43 K as can be seen in figure 19. In sorption, an output temperature of 27 °C is reached at an evaporator temperature of 15 °C thus reaching a GTL_S of 12 K.

Other institutes working on closed transported systems are University of Minnesota, USA, based on CaCl₂ and water working pair [81, 82], as well as University of Applied Science Rapperswil, Switzerland, working with NaOH and H₂O focusing on the improvement of a tube bundle falling film type setup [83, 84].

4 Discussion

Examples from literature for the basic sorption thermal energy storage system designs are presented. It can be seen that there is no uniform approach for testing and evaluation followed in these examples. As a matter of fact, many tests are performed at ideal material temperatures rather than realistic application temperatures. From the pictures provided it is recognised that the systems are all at varying grades of development in term of technology readiness and scale. For these reasons it is impossible to compare the systems on basis of volumetric energy storage density and volumetric charge and discharge power density or even specific discharge output temperature. In order to enable a comparison of systems and especially basic processes as discussed, this study looks into the required GTL_D for desorption, the resulting GTL_S in sorption and its ratio GTL_S / GTL_D , defining the temperature effectiveness TE. This method describes how well the system takes advantage of the full potential of the employed storage material and enables a basic comparison between the systems as well as the basic process designs. Table 2 shows an overview of the reviewed systems. Since some reports provided insufficient indication of water vapour pressure in desorption, these were assumed and indicated in brackets in the table.

Table 2: Overview of the evaluated systems with desorption GTL_D , sorption GTL_S and temperature effectiveness (TE) as the ratio of GTL_S to GTL_D . Values based on assumptions are in brackets.

System	Author	GTL_D [K]	GTL_S [K]	TE [K/K]
Open Fixed	Johannes et al. [58]	(165)	43	0.26
	Tatsidjodoung et al. [44]	(165)	44	0.27
	Michel et al. [61]	62	19	0.31
	Weber et al. [42]	172	42	0.24
	Zhang et al. [62]	(95)	27	0.28
	Aydin et al. [63]	120	21	0.18
	Gaeini et al. [60]	(175)	20	0.11
Open Transported	Nonnen et al. [64]	173	50	0.29
Closed Fixed	Finck et al. [69]	83	30	0.36
	Köll et al. [48]	163	25	0.15
	Palomba et al. [70]	60	25	0.42
	Zhao et al. [72]	67	22	0.33
	Jiang et al. [73]	136	47.4	0.35
	Brancato et al. [71]	60	24.5	0.41
	Yan et al. [77]	154	35	0.23
Closed Transported	Fumey et al. [45]	55	23	0.42
	Zhang et al. [78]	55	22	0.40
	Le Pierrès et al. [80]	43	12	0.28

From table 2 it can be seen that there are substantial performance differences of the systems in terms of TE. In general, it is important to consider that any GTL_D beyond 80 K is not realistic with conventional solar thermal systems or domestic heat pumps. Thus, the respective test results are not directly relevant for the application in buildings.

A performance tendency based on the choice of basic system can be observed. Looking at the open fixed systems, those requiring a GTL_D above 100 K, show a low TE from 0.11 to 0.27. These are systems based on zeolite, which is the most studied solid material for long-term heat storage. In this comparison, these systems are generally larger scale, containing more storage material and are more developed towards the application. This, and the fact that zeolite due to its inherent high porosity is a very poor thermal conductor may lead to these low ratios. The systems with GTL_D below 100 K also have higher TE between 0.28 to 0.31. These work with salt impregnated materials and are generally at a smaller scale. Comparing the open fixed system results to the open transported system result, all but one TE is lower. This points to the tendency of better performance in transported systems due to the continuous process with introduction of fresh sorbent in order to reach high GTL_S . There is a variation of performance in the closed fixed system, again with zeolite based systems requiring substantially greater GTL_D and having lower TE. In part, this has to do with the size of the system as with the open fixed design. Comparing only the zeolite based systems, thus providing a more common ground, it can be concluded that closed fixed systems perform better than open fixed ones and the open transported system reaches a higher TE than the closed fixed system. The comparison cannot be continued to the closed transported approach, since there is no known closed transported system based on zeolite. The closed transported systems are all based on liquid sorbents since these can easily be pumped for transportation. TE is generally higher in this approach in comparison to all other process options.

5 Conclusion

This study categorises sorption thermal energy storage systems into four basic process designs; open fixed, open transported, closed fixed and closed transported. A literature review on process and system designs and performance is composed, following the respective basic process categories. Temperature effectiveness defined as the ratio of GTL_S in sorption to GTL_D in

desorption mode is used as a temperature management performance metric. It is shown that performance of the storage material and hence the exploitation of its potential is dependent on the process design, whereby the transported approach is favoured to fixed bed and the closed system approach performs better than the open one. Over all, the closed and transported system approach is seen to have the highest performance potential in terms of temperature effectiveness. A future challenge to be addressed may thus be mass transport of solid sorbents in closed transported systems.

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