

# Advances in thermochemical energy storage and fluidised beds for domestic heat

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## Abstract

Thermochemical energy storage (TCES) has a vital role to play in a future where 100% of our domestic energy needs are generated by renewables. Heating and cooling represent 51% of total energy consumption, and as such contribute highly to greenhouse gas emissions. As a society, we have effective solutions for this in the form of renewable energy sources, the primary two being: solar thermal heat and wind power. However, one issue plagues these energy sources, that is their intermittency. Specifically, their seasonal deficit which represents a significant energy surplus in the summer months and significant energy dearth in the winter months. Effective seasonal heat storage is needed to solve this problem. At present, one of the best candidates to solve this issue TCES. Both sorption and reaction present many interesting chemical pairings which optimise various different important parameters, including: Energy density, cycle stability, turning temperature, capital and running costs, power output, charging and discharging speed. However, due to hazardous high temperatures and chemicals associated with reaction based TCES, it can be all but ruled out from domestic application. Sorption TCES presents many different promising subcategories, but salt based composite TCES materials are emerging as the most likely category to succeed in a domestic market. Sorption TCES faces one key issue though, that is its power output.

Fluidised bed reactors (FBRs), both bubbling fluidised beds and circulating fluidised beds, have been used extensively in industry to increase the heat and mass transfer of various industrial processes. They have been used in the context of TCES to assist in the charging and discharging of various concentrating solar power plant energy storage systems. And, they have shown to effectively improve the power output of these systems, as well as in other high temperature energy storage systems (sensible energy storage, phase-change energy storage). Overall, it is clear that FBRs have the potential to be applied to domestic sorption TCES to improve its power output, priming it for domestic applications. It is also worth noting

that very few studies exist investigating FBRs in the context of domestic TCES, and there is limited knowledge and understanding one how FBRs will affect domestic TCES systems.

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<b>SYMBOL</b>	<b>MEANING</b>
$\rho$	Density
$H$	Bed height
$\mu$	Viscosity
$U$	Velocity
$d_p$	Particle diameter
$\varepsilon$	Voidage fraction
$\rho_f$	Fluid density
$U_{mf}$	Minimum fluidisation velocity
$Re_{mf}$	Minimum fluidisation Reynolds number
$\rho_p$	Particle Density
$g$	Acceleration due to gravity
$Ar$	Archimedes number
$Re_p$	Particle Reynolds number
$U_t$	Terminal velocity
$h_{max}$	Maximum heat transfer coefficient
$Nu_{max}$	Maximum Nusselt number

<b>GHG</b>	Greenhouse Gas
<b>DSH</b>	Domestic Space Heating
<b>DHW</b>	Domestic Hot Water
<b>PV</b>	Photovoltaic
<b>ST</b>	Solar Thermal
<b>UK</b>	United Kingdom
<b>EU</b>	European Union
<b>Li-Ion</b>	Lithium-Ion
<b>EV</b>	Electric Vehicle
<b>PHS</b>	Pumped-Hydro Storage
<b>TCES</b>	Thermochemical Energy Storage
<b>PCM</b>	Phase-Change Material
<b>MOF</b>	Metal-Organic Framework
<b>ALPO</b>	Aluminophosphate
<b>SAPO</b>	Silico-Aluminophosphates
<b>CSP</b>	Concentrated Solar Power
<b>CaL</b>	Calcium Looping
<b>CCS</b>	Carbon Capture and Storage
<b>ETF</b>	Easy-to-Fluidise
<b>BFB</b>	Bubbling Fluidised Bed
<b>CFB</b>	Circulating Fluidised Bed
<b>FBR</b>	Fluidised Bed Reactor

# 1 Introduction

According to the world meteorological organisation, the 20 hottest years on record have all occurred in the last 22 years [1]. Our oceans are estimated to have increased in acidity by 26% and have also been warming at a rate of  $\sim 0.13^{\circ}\text{C}$  per decade since the beginning of the 20<sup>th</sup> century [2], [3]. In the United States the relative number of extreme weather events has increased since the 1950s [4]. At the same time the atmospheric  $\text{CO}_2$  concentration has increased consistently for the past 80 years, and there is evidence that it has been increasing since the beginning of the industrial era [5]. Global  $\text{CO}_2$  emissions increased by  $\sim 164\%$  from 1970 to 2019, while other greenhouse gas (GHG) emissions increased by  $\sim 41\%$  from 1990 to 2019 [6], [7]. It is estimated that the global subsidies for fossil fuels are double the subsidies for renewable energy sources [8].

Globally, 'Heating and Cooling' accounts for 51% of total energy consumption, and the residential sector accounts for 21.3% of the total energy demand [9], [10]. Meanwhile, modern renewable energy only accounts for 9.8% of the energy supplied for heating and cooling [9]. Solar energy has the highest potential capacity of any current source of renewable energy, and it has been reported that solar energy alone has the potential to meet the world's total energy demand [11]. It is the case that for most residences, throughout the world the solar energy incident on the building exceeds the annual energy demand for domestic space heating and hot water (DSH and DHW, respectively) [12].

## 1.1 European Union and United Kingdom Trends and Policy

Six of the ten most successful countries by growth rate of solar thermal are EU member states. Particularly, Poland and Denmark have shown the most significant market growth recently (179% and 128%, respectively from 2017 to 2018)[13]. The EU is clearly at the forefront of decarbonisation through a shift towards renewables, adopting policies such as the 'Renewable Energy Directive', which sets a binding target of the EU generating 32% of its energy, from renewable resources by 2030 (15% generated from renewable sources in [14], [15]). It is expected that a significant and increasing proportion of this generation will come from domestic level rooftop panels, with the energy production from solar-thermal (ST), and from photovoltaics (PV), quadrupling and increasing by a factor of 16 respectively from 2008 to 2018 (1.15 to 4.38 Mtoe, and 0.64 to 10.57 Mtoe) [15].

The UK supplies 11.6% of its final energy from renewable sources [15]. This is below the EU average, and points to a necessity for an increased commitment to renewables from the UK, although this does not account for viability of certain resources in different geographies. However, positive policies have been introduced. For example: the UK is set to mandate the end of all fossil fuel domestic heating by 2025; this will lead to a clear demand for alternative heating such as solar thermal within the UK market [16]. Solar thermal could be a viable option to help meet these requirements as its conversion efficiency is relatively high and solar fractions (proportion of final energy supplied from solar sources) in the region of 60% are achievable. Fossil fuels are subject to market fluctuations, and so is electricity, no matter if it is generated renewably or not. This inherently decreases the security of these technologies. With the number of excess winter deaths (fatalities) in England and Wales in the winter of 2018 at its highest since the winter of 1976 [17], and 10.3% of households classed as 'fuel poor' [18], there is a pressing need to improve the energy security of many households in the UK .

## 1.2 Global Energy Storage Outlook

Energy storage is perhaps the most important factor influencing the potential contribution renewables can make, as energy must be provided constantly regardless of intermittent nature of renewables [19]. Broadly, energy storage can be broken down into five categories: mechanical, thermal, electrical, chemical, and electrochemical. Some highlighted storage mediums are shown in Table 1. In recent years the clear majority of development in the energy storage sector has been in electrical storage, which has been partially driven by the electrification of various industries. Specifically, the transport industry has seen a large push towards electrification [20]. As a result the most widely utilised storage technology is Lithium-Ion (Li-Ion) cells for electric vehicles (EV) [19], which has outstanding technological readiness and relatively high volumetric energy density ( $\sim 375 \text{ kWh/m}^3$ ). Commercialisation of Li-Ion cells for the EV industry has highlighted the potential for use of these batteries in grid level storage, with several facilities operating currently (the largest of which has a storage capacities of over 100 MWh [21])[19].

Table 1: Grid and domestic energy storage mediums

TYPE	CATEGORY	OUTPUT	POWER RATING (MW)	FULL DISCHARGE TIME (TYPICAL)	DESCRIPTION
<b>PUMPED HYDRO</b> [22]	Mechanical	Electrical	100 - 2500	4 – 16h	Displacement of water to a higher gravitational potential
<b>COMPRESSED AIR</b> [22]	Mechanical	Electrical	10 - 1000	2 – 30h	Mechanical compression of air
<b>FLYWHEEL</b> [22]	Mechanical	Electrical	0.001 - 20	< 1h	Momentum in a rotating massive wheel, typically in a vacuum
<b>SENSIBLE</b> [11]	Thermal	Heat	N/A	< 24h	Temperature difference
<b>MOLTEN SALT</b> [22]	Thermal	Heat/Electrical	1 - 150	< 24h	Thermally stored latently within a phase-change material (Also used in sensible TES)
<b>STEAM ACCUMULATOR</b> [23]	Thermal	Heat/Electrical	10	< 1h	Pressurised steam tank typically applied in solar towers
<b>CAPACITOR</b>	Electrical	Electrical	N/A	Seconds	Electric field; can be used for load smoothing at grid scale

<b>SUPERCONDUCTOR [24]</b>	Electrical	Electrical	5 - 40	Seconds	Cryogenically cooled magnetic field energy storage
<b>SORPTION [11]</b>	Chemical	Heat	N/A	< 24h	Separation of a working pair of chemicals that when mixed sorb and release heat
<b>REACTION [11]</b>	Chemical	Heat	N/A	1-170h	Separation of a working pair of chemicals that when mixed react and release heat
<b>FUEL STORAGE [22]</b>	Chemical	Heat	0.01 - 100 (Hydrogen)	1-170h+	High potential chemicals generated through some means. Hydrogen and syngas are examples
<b>FLOW BATTERY [22]</b>	Electrochemical	Electrical	0.1 - 100	< 24h	Separation of chemicals in solution which exchange ions
<b>LEAD-ACID BATTERY [22]</b>	Electrochemical	Electrical	0.001 - 100	1-8h	Potential difference between lead and lead dioxide
<b>LITHIUM-ION BATTERY [22]</b>	Electrochemical	Electrical	0.05 - 100	1-8h	Separation of some lithium-based compound, and typically graphite which exchange ions

As indicated in Table 1, many other promising storage technologies exist. Pumped hydro storage (PHS) is the storage of energy through the displacement of water from a lower reservoir to higher reservoir during the ‘charging phase’ and converting this gravitational potential by allowing the water to flow to the lower reservoir through a turbine (discharge phase) [25]. In the United States, PHS accounts for the vast majority (86%) of energy storage at the utility scale [26], and in the EU PHS is by far the largest energy storage reservoir [27]. PHS has the advantage of a very fast response time, of the order of seconds, as well as a high power output (1-2 GW)[25]. This is far larger than currently installed electrical battery storage



facilities (with the largest installed Li-Ion storage facilities reaching only 100 MW [21]). It is therefore likely that PHS will play a significant role in large grid scale energy storage.

### 1.2.1 Current Thermal Energy Storage Development

Thermal energy storage is energy stored directly in the form of either sensible, latent heat, or energy stored through the separation of chemicals which, when recombined, release heat. Many domestic households have a sensible heat storage system in the form of a hot water tank. Also, sensible heat storage can be used to provide heat on a district scale, e.g. in steam accumulators or low grade sensible industrial waste heat [11]. However, all thermal energy storage systems will cool down over time and require significant insulation to extend their usability [11]. A typical sensible energy system (like that studied by Rezaie et al. [28]) has an energy efficiency of 60%. Latent heat storage is based on the phase change of a material, typically being solid-liquid or liquid-gas. Latent heat will typically have a much higher energy density than sensible heat (although this is of course highly dependent on the material), and can be stored for longer periods due to the lower thermal gradient and conductivity [29]. However, this also means that charge and discharge rates can be low. On a grid level, sensible heat systems based on molten salts are typically used to store thermal energy, while latent heat phase change materials (PCM) are applied for domestic and residential heat demand and in the thermal management of electrochemical batteries using mainly organic materials (paraffins, fatty acids) [29], [30].

As with most renewable sources of energy, one of the most important issues facing solar thermal energy is the intermittency of the resource. To achieve high solar fractions, some form of energy storage must be employed since solar irradiance is not available for extended periods. During the night, no solar irradiance is available, and importantly several areas in the world experience prolonged periods of low solar irradiance due to cloud cover and seasonal climatic conditions. This intermittency can be addressed using diurnal sensible heat storage in the form of water heat storage, which is commonly used, non-flammable, non-toxic, easy to install, and importantly has a high specific heat capacity. However, recently, latent heat storage (mainly PCM) has begun to gain commercial traction as a method to store heat for domestic hot water and space heating. Latent heat storage has a typically high storage capacity (heat of phase change compared with specific heat capacity per °C), and thus the energy storage density of PCM can be very high at temperatures close to the PCM phase transition temperature, making it a good candidate for seasonal thermal energy storage [11]. However, neither of these energy storage methods are good candidates to effectively store thermal energy for long periods (e.g., months) of time without large amounts of insulation as both typically need to be stored at temperatures above ambient if they are to be used for DHW and DSH. Thus, there is a need for novel domestic seasonal thermal storage technologies which can be categorised as illustrated in Figure 1. Thermochemical energy storage is a promising technology that could significantly increase solar fractions of a domestic solar thermal system by directly addressing the seasonal thermal energy deficit. This potential can also be extended to other heat generating renewables, significantly increasing their energy fractions by limiting their intermittency. The technology could significantly reduce losses and make the stored thermal energy available over long periods, as the thermal energy is stored at ambient temperature and therefore has low potential for thermal losses [31].

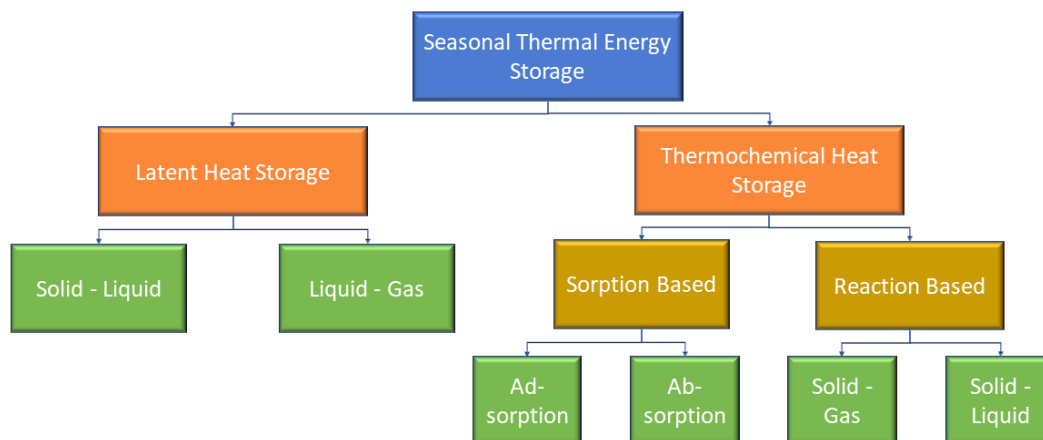


Figure 1: Seasonal energy storage methods

Both latent and thermochemical storage have sub-categories. For latent heat storage, these categories are based on the phases involved in the transition. Solid–liquid is based on the thermal energy absorbed or released by liquification or solidification. Liquid-gas is based on the thermal energy absorbed or released by evaporation or condensation. Examples of well-developed solid-liquid phase change materials (PCMs) include: ice, paraffins, fatty acids, esters, salt hydrates, and metals [29], [32]. These will have various different applications based in part on their phase-transition temperature. This is the temperature at which the material changes from a solid to liquid or liquid to gas, and it is the point at which energy is stored in its latent form. Liquid-Gas latent heat methods are rarely used due to the high pressure, and large volumetric variation associated with the phase transition [33]. In the case of thermochemical energy storage, this category can be further categorised as sorption-based storage, and reaction-based storage. Reaction based methods take advantage of reversible chemical reactions which release heat during one reaction (exothermic) and absorb heat when undergoing the reverse reaction (endothermic) [34]. These methods typically involve a pair of compounds which separate in the endothermic reaction and combine in the exothermic reaction. Thus, heat is stored at ambient temperature when both compounds are kept separate from one another. Reaction based thermochemical energy storage methods include: ammonia based reactions, metal hydride dehydration, and carbonate decarboxylation [34]. However, these reaction-based methods typically have endothermic temperature ranges exceeding 150°C (and can be higher than 1000°C), or involve toxic and dangerous chemical combinations, and thus can be unsuited to domestic thermal energy storage. Sorption based thermochemical energy storage methods are typically utilised at lower temperatures and can often use water as one component of its working pair, thus reducing costs, toxicity, and volatility. As such, it is much better suited to domestic and residential applications, and particular focus has been given to its potential as a domestic scale solar thermal heat storage medium.

### 1.3 Energy Horizon and Microgeneration

With the successful commercialisation of the Tesla Powerwall, Samsung SDI ESS, and LG Chem's RESU batteries, there is a clear momentum towards 'at home' consumer level electrical storage and generally toward domestic microgeneration. This is further compounded by the fact that electric storage capacity is set to triple by 2030 if current trends continue [35]. This has been driven in a large part by improved technologies such as smart metering which allows consumers to monitor their usage and peak costs. Consumers now also utilise domestic level storage to engage in peak shaving, which can reduce costs [36]. The success and rise of domestic scale PV, and to a lesser degree domestic scale wind power, also now opens the possibility for households to sell back to the grid when generating an excess (although this is dependent on the local grid policy), but also to store this excess. From this, it is clear that the future of domestic electricity production and storage is a holistic one, where the grid will be used in combination with domestic storage.

Conversely, DHW and DSH are not connected to any 'heat grid' and cannot be traded in the same way. And while in a gas boiler, heat is typically generated domestically, the fuel is not generated domestically. Solar thermal energy conversion is typically much more efficient than solar PV in terms of DHW and DSH (with typical PV cells achieving a conversion efficiency of 15% to 20% in terms of irradiance to voltage [37]), and yet solar thermal only represents 0.7% of global heat consumption [38], [39]. This is likely due to an assumption that electrification is the best option when it comes to decarbonising domestic heat generation, however if the future is to involve a large proportion of domestic power generation then roof space will be limited [40]. With the lower efficiency of PV, it will require much more area to generate the necessary energy to heat homes, while solar thermal panels could achieve the same result with a fraction of the area. However, it is not yet clear which technology (PV or ST) will prove to be more economically viable. Previous research comparatively assessing the economic cost of PV and ST has found that ST has an advantage. However, there is future potential for PV equal this advantage, especially in colder climates [41]. As stated previously a key issue constraining solar thermal, and renewables in general is storage. Electricity from renewable sources can be both traded and stored locally but has low conversion efficiency; if the full potential of heat from solar is to be realised, effective means of either storage (or trading) are required.

This review will focus on first looking at the recent progresses in the field of TCES. Looking first at system types, and then at materials for TCES. These materials will be reviewed, highlighting key metrics useful to domestic energy storage. The key metrics looked at will be energy density (gravimetric and volumetric), turning temperature, power, efficiency, and number of cycles. All of these factors are vital to the success or failure of a storage medium, but we will pay particular attention to the power output metric. These metrics will allow for informed decisions making to be made on the chemicals best suited for domestic thermal energy storage. It should be noted that as we are reviewing thermal energy storage, we will not be discussing forms of energy storage such as redox flow batteries, Li-ion batteries, and other energy storage mediums which could be applied in the setting of domestic heat. This is because these storage mediums have little to gain from the addition of fluidised bed reactors. The review of the field of TCES will then be looked at in the context of fluidised bed reactors, in order to assess the feasibility, and potential of these advanced reactors to improve the aforementioned key metrics. The second part of the review will focus on studies undertaken in the field of energy storage when utilising fluidised bed reactors, paying

particular attention to the use of fluidised beds in high-temperature TCES, a field that has already seen significant investigation. As well as looking at how FBRs have been used in sensible and PCM based heat storage methods. From this literature the review will assess and draw conclusions on the state of art of fluidised bed reactors paired with thermal energy storage and make recommendations as to the approach that key stakeholders should take in order to drive the decarbonisation of domestic heat. While several review articles are present in the field of thermochemical energy storage, there is an apparent gap of reviews of investigating the emerging field of fluidised beds in thermochemical energy storage. This is especially relevant due in first part to: the potential improvement to certain key metrics of thermochemical energy storage systems employing fluidised bed reactors which has been identified by a few researchers; and in second part: the apparent lack of relevant research [42]–[44].

## 2 Advances in Thermochemical Energy Storage Systems

Thermochemical energy storage (TCES) is a way of storing energy through the exploitation of reversible chemical and physical reactions. A TCES system can be thought of as an analogous ‘heat’ battery. The most basic TCES system is comprised of a working pair of two chemicals (A, B), a store for each of these chemicals, and a reactor. When energy is required from the system, these two chemicals are reacted together, releasing energy in the form of heat. When energy is to be stored, energy (again in the form of heat) is added to the reacted chemicals to chemically or physically separate them. This generic reaction under specific thermodynamic conditions at the point which they are stored in separate forms is shown in Equation (2.1).



One of the key benefits of a TCES system is that it can theoretically store energy indefinitely, which offers a huge advantage over other thermal energy storage systems. TCES is therefore a potential technology for seasonal energy storage, and theoretically allows for 100% of required thermal energy to be generated using renewables. As well as this it offers the highest energy storage density (by mass and by volume) of any thermal energy storage technology [11]. However, the field is still in its infancy with few examples of successful commercialisation. In recent years considerable research efforts have focuses on material development, reactor design, and material optimisation [34], [45]. There are many categories of TCES, and many working pairs within these categories. Despite this, no category or working pair has yet been commercialised in the context of domestic heat.

### 2.1 Sorption

Sorption storage refers to a TCES system where the working pair acts endothermically by breaking the chemical or physical bonds of the chemical pairs (physical, referring Van Der Waals force bonds, and chemical, referring to covalent bonds), and acts exothermically when these chemicals resorb in reverse [45]. This category of TCES is typically divided into adsorption and absorption, both of which have their own unique benefits and characteristics. When comparing sorption to reaction based TCES, it can generally be said that sorption systems have the advantage of the high technological maturity, utilising cheap, and non-toxic materials with high abundance for its working pair. The temperature range is typically <500°C, however the energy density is typically lower compared to reaction TCES [46].

In general, adsorption is a process that occurs at the surface, while the absorption refers to a process where the material is fully retained and taken up by the bulk of another [47]. During adsorption, an ‘adsorptive’ is bonded to the surface of an ‘adsorbent’ owing to either physical or chemical forces, at

which point the ‘adsorptive’ is referred to as ‘adsorbate’ [48]. The reverse process of the adsorption, known as desorption, is the step when the ‘adsorbate’ leaves the surface of the ‘adsorbent’ as graphically demonstrated in Figure 2. The adsorption can be split into two broad categories: physisorption and chemisorption. The former is driven primarily by van der Waals forces, whereas the latter is driven primarily by covalent forces [49], [50].

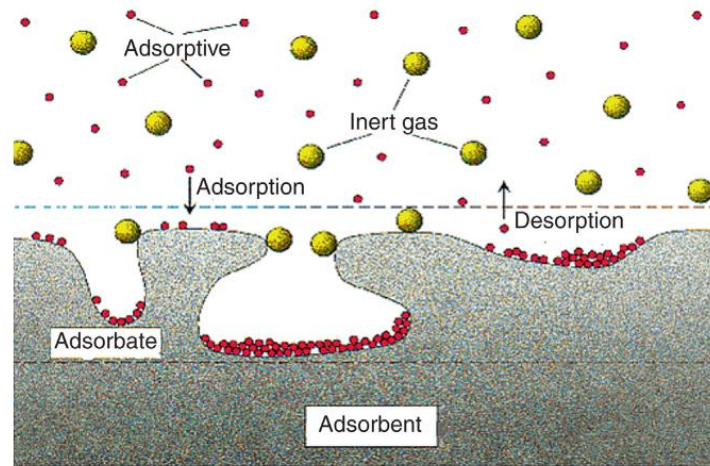


Figure 2: Adsorption and desorption of an adsorption based TCES material [34]

The equilibrium of an adsorbent-adsorptive system is typically described by adsorption isotherms, which typically plot the ‘amount adsorbed’ against ‘relative/partial pressure’ at a constant temperature [51]. Naturally, the kinetic energy and frequency of collisions increase with temperature and so effect the amount of adsorbate which can be adsorbed [52]. Figure 3 demonstrates an ideal physisorption thermal storage system on a Clausius-Clapeyron diagram. Here, the adsorbate is shown to the left of the plot, and the adsorbent to the right. At the beginning of the storage phase (point A), the adsorbate is desorbed from the adsorbent through a heat addition,  $Q_{in}$ . Once the desorption process has been completed, the adsorbate can then be taken down to  $T_e$  and  $P_e$  (typically ambient conditions), allowing the recovery of the condensation heat of the adsorbate (*i.e.*  $Q_{cond}$ ). Heat can then be stored indefinitely (point B), assuming the adsorptive and adsorbent are perfectly separated. The heat can be released by allowing the adsorption process to take place, (*i.e.*  $Q_{out}$ ). In order to begin the storage phase again, heat needs to be added to the adsorbate/adsorptive in order to evaporate it (*i.e.*  $Q_{evap}$ ). Once the adsorptive has reached the required pressure and temperature ( $T_c$  and  $P_c$ ), the storage process has completed one full cycle. It should be noted that  $X_{eq,1}$  and  $X_{eq,2}$  represent lines of constant mass.

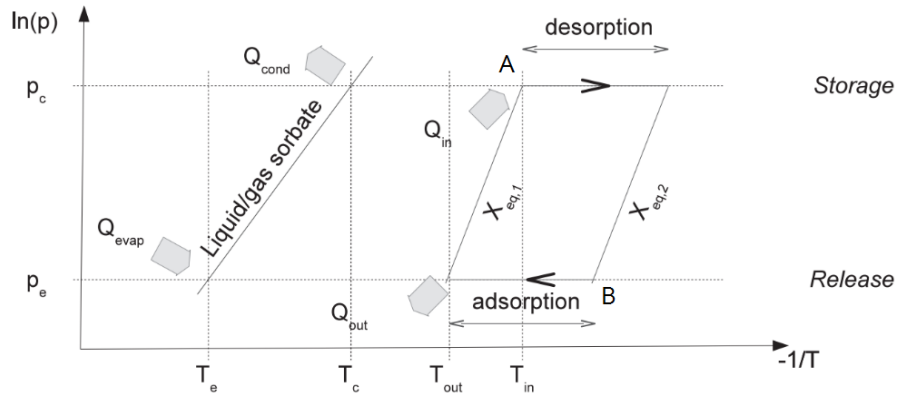


Figure 3: Ideal Clausius-Clapeyron sorption cycle for adsorption based TCES material pair (gas/liquid adsorbate) [53]

In the case of physisorption, the vast majority of working pairs are comprised of a molecular sieve and a gas or liquid [45]. In general, this gas or liquid is steam or water as it is abundant and non-toxic. Physisorption systems can therefore be ‘open-cycle’ (Figure 4), where moisture from the ambient air can be used as the water in the working pair [54]. This can increase the energy density of the TCES system as there is no need for a water store. However, in this case, the storage density is highly dependent on ambient conditions, such as air humidity.

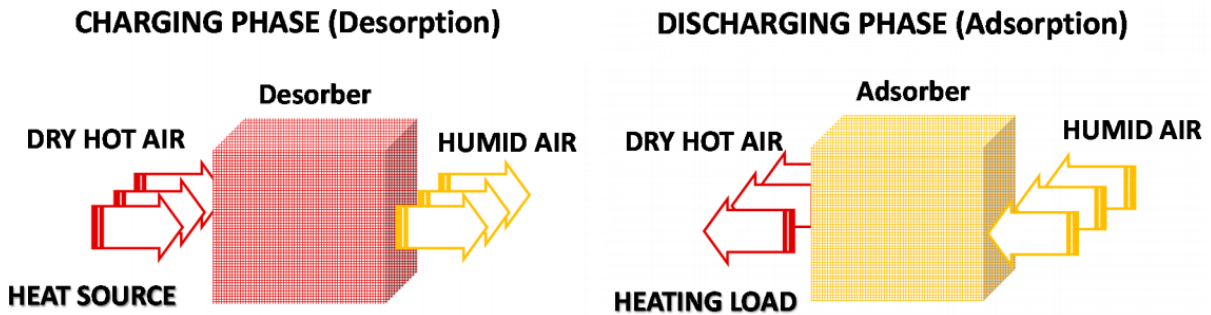


Figure 4: Open system diagram for an adsorption based TCES system (Adapted from Vasta et al. [54])

A closed system is a system which stores both working pair chemicals and does not utilise any chemicals from the environment (Figure 5). These systems are often more complex but can take advantage of the heat of condensate of the gas or liquid adsorbate, which would otherwise be returned to the environment. Unlike in an open system (where the heated sorbate is used for whatever application



needed), the closed system relies on a heat exchanger between the bed (adsorber/desorber) and the heat load.

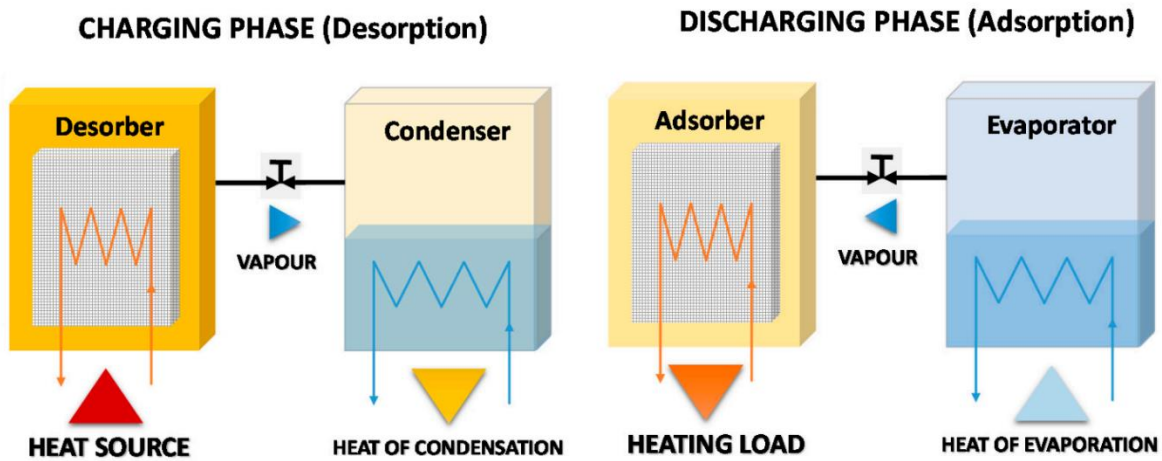


Figure 5: Closed system (Adapted from Vasta et al. [54])

Absorption (bulk sorption), is typically considered as a process where liquid or gas is ‘taken up’ by the bulk material [46], [47]. In most cases (especially in thermal energy storage) within the TCES, the absorption refers to a combining of a certain chemical into liquid water [45]. The most prevalent TCES material that utilises bulk sorption is hygroscopic inorganic salt, where the hydration of this salt leads to a significant exothermic reaction [34], [55]. In general, the hydration and dehydration of these salts are comprised of nucleation and growth reactions [56], implying that the energy release from these salt hydrates during hydration process can be slow at near-equilibrium conditions [57].

One interesting property of salt hydrates is their ability to be impregnated into porous materials. This property opens the door to the development of a composite materials, where both the surface sorption properties of molecular sieves and the bulk sorption properties of hygroscopic salts can be utilised to improve the energy density of a TCES system [34].

### 2.1.1 Zeolites

One key group of TCES materials are zeolites. zeolites are a type of mineral largely comprised of aluminium, oxygen, and silicon. They have a porous structure, and as such can adsorb liquids or gases. Many types of zeolite exist, with 252 known structures to date [58]. They vary based on the presence of other constituents (for example, titanium, tin, and zinc), and based on their microscopic framework. Among the zeolites applied to TCES, the most widely used types are 4A and 13X [54]. Like most molecular sieves, zeolites can be adsorptive depending on partial pressure and temperature. Although, research by Kato [49] has ruled out zeolites from the candidate group for seasonal TCES due to their relatively high cost.

A study by Dicaire and Tezel [59], and a study by van Alebeek et al. [60] investigated water and zeolite 13X as a working pair in a TCES system. While in the initial study by Dicaire and Tezel [59], a global thermal storage efficiency of between 50% and 60% was achieved, van Alebeek et al. [60] were able to achieve an efficiency of 76%, with a potential increase to 91% if the sensible heat can be recovered. This difference in efficiency can be attributed to the lower regeneration temperature in the study by Dicaire and Tezel

[59] (when compared to the study authored by van Alebeek et al. [60]), but also due to the differences between the reactors used in both studies. Dicaire and Tezel [59] achieved an energy density of  $\sim 200$  kWh/m<sup>3</sup>, while van Alebeek et al. [60] only achieved a material energy density of 136 kWh/m<sup>3</sup>. It should be noted that this is still above the highest achieved energy density in PCM energy storage (Sodium acetate trihydrate, 113 kWh/m<sup>3</sup>) [29]. Relative to other storage materials, these energy densities are low, and consistent with the earlier studies that zeolites alone are not suitable for seasonal TCES. Köll et al. [61] also investigated zeolite 13X and water as a TCES working pair; This study explicitly investigated if this pair were suited to seasonal TCES, and if zeolites in general were suited to seasonal TCES. In this study, an energy density of 178 kWh/m<sup>3</sup> was achieved. The system designed was sized to provide DHW and DSH for a single domicile. With a volume of zeolite equal to 6 m<sup>3</sup> and a collector area of 12 m<sup>2</sup>, a solar fraction of 83.5% was achievable over a year, using solar collectors (based on 2015-2016 heating period in Gleisdorf Austria), which is clearly very promising however the storage volume is large, perhaps to the scale that it is unsuitable for domestic applications. Another key issue with pure zeolite based TCES is its power output. Large-scale projects such as the MODESTORE project, and the MONOSORP project have only achieved peak power outputs of  $\sim 1$  kW [62] and 1.8 kW [63]. Johannes et al. [64] achieved a power output of 2.25 kW, but this is the highest power output available in literature of a purely zeolite TCES. Obviously, this is not sufficient power output for a direct demand for many processes in a household. These previous reports indicate that the TCES system needs another source with higher power output potential to transfer heat energy through (such as a hot water tank), which will incur heat losses, reduce the thermal efficiency, and increase system complexity.

### 2.1.2 Metal Organic Frameworks

Metal-organic frameworks (MOFs) are a type of polymer-based adsorbent material consisting of metal ions surrounded by organic linker molecules. They are at the forefront of material research in the field of molecular sieves, and more than 20,000 structures are known [65]. They can be adjusted and tuned to optimise characteristics, and are typically designed with a specific surface area of higher than 2000 m<sup>2</sup>/g [54]. This large surface area leads to increased adsorption potential and thus increased energy storage density. These highly tuneable characteristics allow MOFs to maintain high energy densities at low charging temperatures. Elsayed et al. [66] found that CPO-27(Ni), has a much higher gravimetric energy density than that of the zeolite 5A at the same charging temperature (612.72 kJ/kg, and 228.24 kJ/kg, respectively). Bon et al. [67] has identified several MOF-based adsorbent which are highly promising in their previous report. The most up to date water uptake values ( $G_{H_2O}/G_{ADS}$ , mass of water uptake per mass of adsorbent) of these promising MOFs and other selected MOFs are shown in Table 2. More research is needed to practically calculate the energy density of these materials, although obviously water uptake is proportional to energy density.

Table 2: Promising MOFs for TCES

MOF NAME	MAX WATER UPTAKE ( $G_{H_2O}/G_{ADS}$ )	STUDY
CAU-10-H	0.35	[68], [69]
MIL-160	0.40	[70]
CPO-27(NI)	0.47	[71]
AL-FUMARATE	0.53	[71]
MOF-808	0.74	[72]
CR-MIL-101	1.26	[72]



Despite these highly promising values, this is a relatively new research area and many of these materials are currently only produced in small, laboratory-scale batches [66]. Clearly, MOFs are a strong candidate for the future of adsorbent materials, despite their high production cost which has been shown to be in the range of 35 – 71 \$/kg [73]. However, until they can be produced in large batches at competitive costs (Zeolite 13X based space heating systems can achieve a cost per energy released of 5.4 - 6.1 ¢/kWh [74]), the materials will remain difficult to study and to commercialise [75].

### 2.1.3 Silica Gel

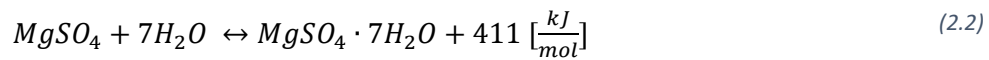
Silica gel is a material comprising of a framework of silicon and oxygen. Like zeolites, this framework has a highly porous surface and acts like a molecular sieve. Due to their low cost and abundance, they have historically been employed as materials for water adsorption, leading to an application as an absorbent material of the TCES system. Jaehnig et al. [76] investigated silica gel for a TCES system to provide DSH in a single family house. The study found the energy density to be much lower than expected. Subsequent studies have demonstrated that the energy density of silica gel is lower than the sensible energy density of water (160-180 kJ/kg, compared to water with a typical temperature lift of 50K, which results in an energy density of ~210 kJ/kg) [62], [54]. Silica gel has, however, been shown to have a good cycling stability, losing negligible energy storage capacity over 10 cycles, as is shown by Ait Ousaleh et al. [77]. Clearly, silica gels alone are not suitable for seasonal TCES due to their low energy density. Nonetheless, they should still be considered though as a host material for more energy dense materials owing to their low cost and their high cycling stability, leading to the material showing potential when it comes to composite based TCES [78].

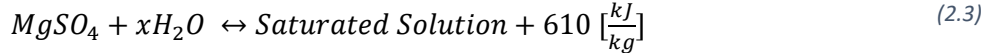
### 2.1.4 Other Molecular Sieves

In recent years much of the material research in the area of molecular sieves has been in the development of synthetic materials such as aluminophosphates (ALPOs), silico-aluminophosphates (SAPOs). These materials have exhibited very high levels of water vapor exchange, and thus have high potential as TCES materials. Initially, ALPOs were found to be competitive with zeolites in terms of energy density [79]. However, the first studies into SAPOs reported a storage density only marginally higher than silica gel (5.7% increase), despite the large moisture uptake potential [80]. This coupled with the high cost of research and development of these materials would likely explain the lack of interest in these materials as serious candidates for TCES. However, like previous materials they certainly have significant potential as host matrices for other TCES materials.

### 2.1.5 Salt Hydrates

Salt hydrates are different from the previously discussed storage materials since they do not adsorb but do absorb (bulk sorption) their liquid/gas partner. These salt hydrates function in two ways: i) Hydration reaction where a charged substance (*i.e.*, salt) combines with water, forming a stable hydrated salt with discharged state (see an example for magnesium sulphate monohydrate in Equation (2.2)[81]). This reaction is typically a solid-gas reaction with gaseous water vapours hydrating the salt; ii) The second possible reaction is dissolution of the salt into the water if there is a high enough relative pressure of moisture. Unlike the first reaction, this reaction is a solid-liquid reaction having a H<sub>2</sub>O in form of liquid water (see deliquescence/efflorescence reaction in Equation (2.3)[82], [31]).





However, in TCES, the hydration reaction is usually the one used, as various issues can be encountered during its deliquescence reaction. For instance, a liquid film on the surface of the salt can slow or prevent the reaction, and the salt solution can cause significant corrosion to other components in the system [75], [83].

Yu et al. [75] suggested magnesium sulphate ( $MgSO_4$ ) as a candidate of the salt-sorption working pairs in their review of sorption TCES for solar energy. Donkers et al. [55] reviewed 563 salt hydrate reactions to assess which best suits seasonal domestic scale TCES. In principle, the authors narrowed down the salts based on their turning temperature (difference between the temperatures of dehydration and hydration) and their energy density. Factors such as price, safety, and stability were also considered. The study concluded that potassium carbonate ( $K_2CO_3$ ) and magnesium chloride ( $MgCl_2$ ) are the best suited salts. However, they also concluded that no ideal salt can be chosen since the study conducted under unrealistic boundary conditions (*e.g.*, one cycle per annum, and reliance on pure salt hydrates). N'Tsoukpoe et al. [84] also reviewed 125 salt hydrates for their low temperature TCES application. This study first sorted the salt hydrate based on the safety, the hydration and dehydration characteristics, and then energy density and turning temperature. This study concluded that Strontium bromide ( $SrBr_3$ ), Lanthanum chloride ( $LaCl_3$ ), and Magnesium sulphate ( $MgSO_4$ ) salts are the most promising materials. The authors suggested that strontium bromide and lanthanum chloride would be the best suited if cost were disregarded; however, consequent economic analysis indicated that magnesium sulphate may be favourable. Totally different conclusions reached by Donkers et al. [55] and N'Tsoukpoe et al. [84] lends credit to the idea that the ideal salt for this application has not yet emerged. However, these studies are certainly useful in order to narrow the field of potential salts. Fernández et al. [85] attempted to narrow down the candidates further and assessed the strontium bromide and the magnesium sulphate for their corrosion characteristics in a TCES system. The study revealed that the strontium bromide would corrode through carbon steel at an unacceptable rate but slower than the magnesium sulphate through aluminium and stainless steel. However, more salts are needed to be tested to evaluate their corrosiveness, since this data is clearly useful for the design of complex reactors (closed, fluidised bed, moving bed) which likely have a high contact area with the salt. The most promising salts with important data given by Donkers et al. [55] can be found in Table 3.

Table 3: Selected salts with relevant data [55]

Salt	Volumetric energy density (kWh/m <sup>3</sup> )	Hydration temperature (°C)	Dehydration temperature (°C)
<b>K<sub>2</sub>CO<sub>3</sub></b>	361.11	59	65
<b>SrBr<sub>3</sub></b>	552.78	48	54
<b>MgSO<sub>4</sub></b>	630.56	24	28
<b>LaCl<sub>3</sub></b>	669.44	48	158
<b>MgCl<sub>2</sub></b>	866.67	61	214

As many of the reviews and studies within the area of salt based TCES have indicated, the optimum salt is not yet clearly identified. The ideal salt is not only one that has the highest energy density, including but also not limited to favourable temperature range, low toxicity, high cost-effectiveness, low corrosiveness

and high stability. The emergence of composite materials incorporating both salts and molecular sieves has further complicated the question. There is now the potential for different characteristics to exhibit themselves in different reactor types and there is clearly much research to be done for seasonal TCES applications.

### 2.1.6 Composites

Composite materials are having significant potential for sorption based TCES. A composite material made of host matrix impregnated (shown in Figure 6) with another sorbent material can take advantage of the sorption capacity of both materials. Likewise, the favourable characteristics of one material can be taken advantage of, and the composite can exhibit a synergetic effect on performance. Hygroscopic salt, impregnated into a microporous matrix (Zeolites, MOFs, silica gel), is the most common form of composite material [54]. To the best of our knowledge, the first composite material study was reported by Aristov [86], who attempted to take advantage of the high sorption capabilities of various salts in combination with silica gel as a host matrix in order to prevent agglomeration of the salt, which impeded mass transfer. This study demonstrated the benefits of composite materials and an extensive study by various groups in the area followed.

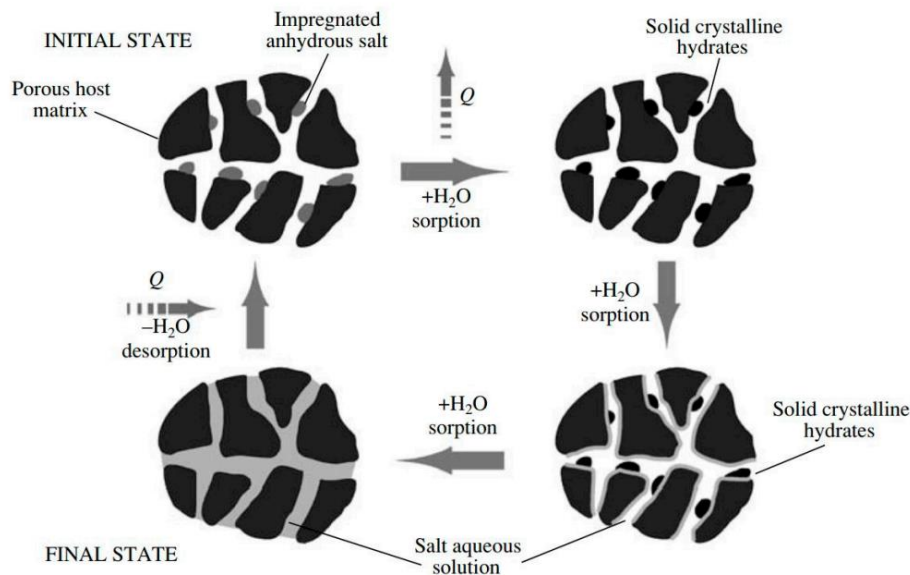


Figure 6: Composite sorbent working principle [86]

Hongois et al. [87] was the first to study the feasibility of the composite sorbents for seasonal TCES applications. The study examined the potential energy density of a composite material utilising zeolite 13X as the host matrix, and magnesium sulphate as an impregnated hygroscopic salt. While this initial study only demonstrated an energy density of  $166 \text{ kWh/m}^3$ , this is still significantly higher than case with zeolite 13X alone ( $131 \text{ kWh/m}^3$ ). Unlike the pure salt based TCES, this composite did not experience any severe agglomeration. A study conducted by Casey et al. [88] reviewed 20 combinations of matrix and salt for an open TCES system. This study assessed the composites based on their energy density, and sorption capacity in a working temperature range of  $30 - 140^\circ\text{C}$ . It was concluded that, vermiculite impregnated with calcium-chloride and with lithium bromide are the best candidates for this system. This conclusion was based on the finding that these two composites had comparatively high volumetric energy density ( $49.51 \text{ kWh/m}^3$  and  $46.31 \text{ kWh/m}^3$ , respectively) as well as good time to equilibrium moisture content.

However, the one impregnated with magnesium sulphate exhibited the highest gravimetric energy density (406.5 kJ/kg) but was discounted based on its poor vapour sorption isotherms, also the material had a low bulk density which lead to a low volumetric energy density (38.39 kWh/m<sup>3</sup>). However, the limit of this study is that the materials were only characterised here in a hydration test bed and were not tested in an actual TCES reactor. S.Z. Xu et al. [89], [90] and J.X. Xu et al. [91] tested Zeolite 13X impregnated with magnesium sulphate, and magnesium chloride, respectively. An energy efficiency of 66% was achieved using a magnesium sulphate composite under turning temperature range of (90-250°C). An energy density of 123.4 kWh/m<sup>3</sup> was also found experimentally. J.X. Xu et al. [91] took advantage of both reactions in Equations (2.2) and (2.3). This study tested a material which not only took advantage of the moisture adsorption of the zeolite, and the hydration of the hygroscopic salt, but also deliquescence of the salts into the solution to increase the energy density of this material (Figure 7). An energy density of 308 kWh/m<sup>3</sup> was reported by J.X. Xu et al. [91] and is to the best of the authors' knowledge the highest among the composite TCES materials reported so far, and the closest to the theoretical maximum of 694.44 kWh/m<sup>3</sup>, calculated by van Essen et al. [92]. The concept of multi-step sorption has only been demonstrated. The impact of incorporating both deliquescence and salt hydration in the same composite has not been investigated past this initial study yet, but these initial results clearly indicate a potential increase in the storage capacity making these composite materials promising candidates for inter-seasonal TCES.

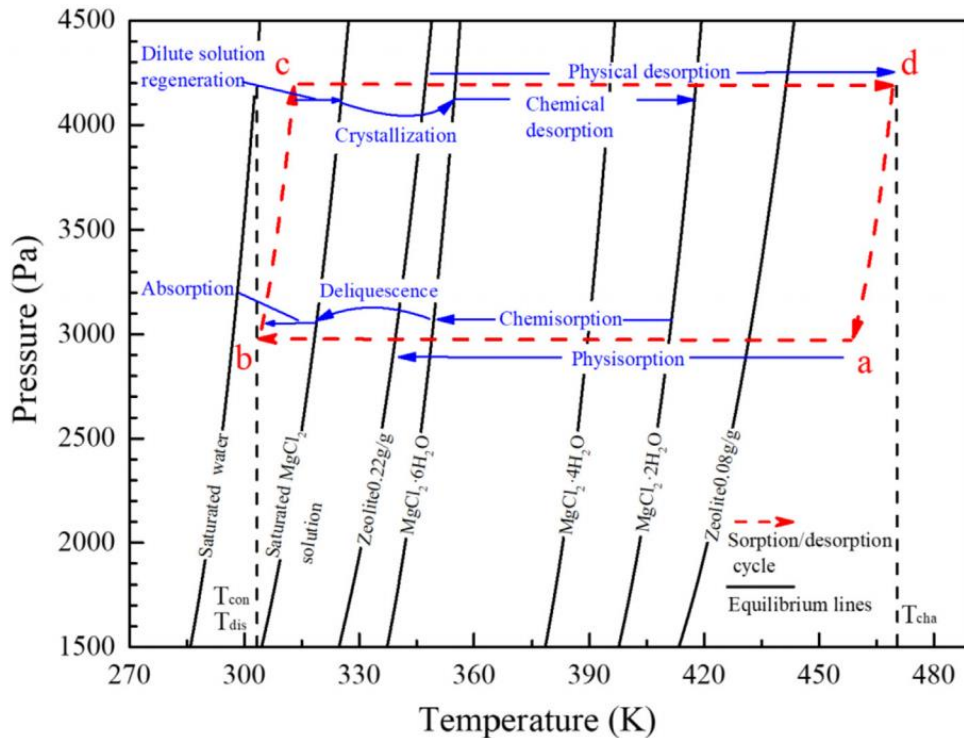


Figure 7: The Clausius-Clapeyron phase diagram of a multi-step sorption process of MgCl<sub>2</sub> and zeolite 13X composite [91]

Similar to the pure salt hydrate TCES case, the composite-based TCES also requires more investigation before wide implementation. Specific investigation of MOF interaction with salt impregnation would be

beneficial to the field, as MOFs have the potential to be tuned extensively to meet the required properties of a host matrix. Attention to how these composite materials perform in certain advanced reactor beds, such as moving or fluidised beds, would be highly beneficial. Pure salt hydrates cannot perform in these types of beds due to their agglomeration characteristic.

## 2.2 Reaction

Pure reaction based TCES differs in many ways from sorption technology. The distinction is perhaps a wrong one to make as the word 'sorption' could arguably be used to describe the process of reaction based TCES. Difficulty arises because chemical storage by its definition represents the chemical change of the material. This could include salt-based storage, as clearly the chemical structure of a salt is changed in hydration and deliquescence. Thus, there is an argument that sorption storage can include all forms of TCES, while the reaction storage can include all apart from pure adsorption TCES. For the sake of clarity, classification of adsorption and water-salt based absorption storage as sorption storage is widely accepted [93]. With the term 'reaction-based TCES', referring to reversible chemical reactions, which typically do not use water as a component of the working pair.

The fundamental theory of reaction TCES does not differ from that of other TCES systems. Typically, reaction TCES systems are studied in the context of Concentrated Solar Power (CSP) [94], because the reaction TCES involves toxic materials (for example, cobalt-oxides, ammonias, sulphur-oxides), and their high turning temperatures (>1000°C, in many cases) is also another reason. These drawbacks mean this type of system cannot be used in an open system and is unsuited for small scale domestic use. Only a few attempts have been made to apply reaction TCES to domestic seasonal energy storage applications [95], [96], [50]. Reaction TCES, however, offers the highest energy densities of any TCES type with material offering energy densities as high as 2050 kWh/m<sup>3</sup> (i.e., calcium-hydrides) [94]. It also outperforms PCMs in the context of CSP with regard to peak temperature (<900°C for the highest melting temperature of PCMs [97], with molten salt being limited to ~550°C [94]).

Three major classes of reactions have been investigated in the context of TCES: Ammonia based reactions, dehydration (referring to the removal of hydrogen not H<sub>2</sub>O) of metal hydrides, and decarboxylation of carbonates [34]. Beyond the development of materials and characterization of the reaction kinetics, research focuses on the design of the chemical reactors looking to improve stability, energy density, and efficiency of the system. Reactors can be classified according to the number of material phases present, whether the process is continuous or batch, whether the process is isothermal or adiabatic, whether the reactor is stationary or moving [93]. A reactor chamber can put into contact gaseous and solid phases through a stationary or a moving bed of particulate material. A fixed bed, akin to a plug flow ideal reactor, is a simple design that allows a high conversion. However, without any ability to mix the solids, a fixed bed cannot easily dissipate heat and so they are prone to significant reaction hot spots and hindrance of mass and heat transfer [93]. Mixing the solid phase is obtained either mechanically, or through fluidisation of the solids in the flow of gas. Several types of moving beds exist, for example, conveyer driven, screw beds, rotary beds, and other gravity assisted beds. Both moving and gas-solid fluidised beds can be further classified according to how heat is delivered to or extracted from the solid phase: within the fluidising fluid or throughout some heat exchange pipes; and how the particles are circulated.

### 2.2.1 Ammonia Based

In the case of high temperature ammonia based reactions, Dunn, Lovegrove, and Burgess [87] reviewed this area [98]. This review was concerned mostly with reversible ammonia dissociation shown in Equation (2.4).



The chemicals used in ammonia based TCES are highly abundant (nitrogen makes up the majority of the atmosphere, and hydrogen can be synthesised from water using electrolysis). This reaction also has a very high molecular heat when compared to most adsorption-based systems, and as such would represent a much higher energy density, which would be useful in the domestic market where space is at a premium. However, the toxic nature of the chemicals and the hazard of storing large amounts of pressurised toxic and flammable materials represent a serious concern in a domestic setting. For these reasons, this reaction has only been utilised to produce electricity from CSP. The typical layout of an CSP ammonia dissociation plant is shown in Figure 8. As shown in the figure, an ammonia dissociation plant functions by dissociating ammonia into hydrogen and nitrogen gas and stores these gases separately during the charging step. During discharge, ammonia is synthesised from the gases, which generates high temperature heat to drive a steam turbine, which generates electricity.

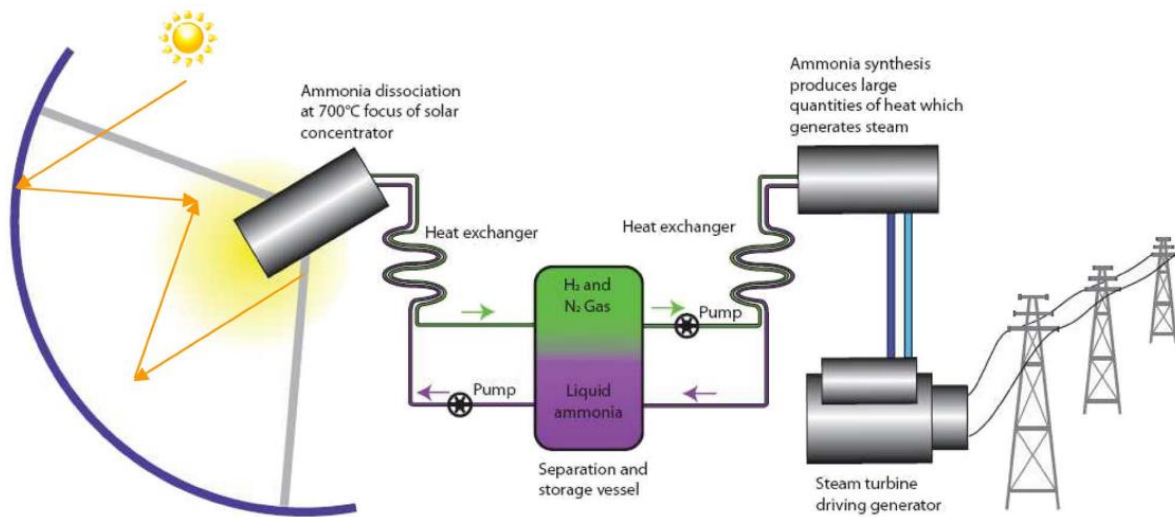
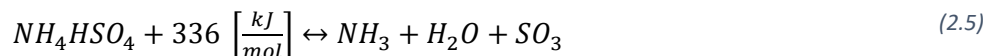


Figure 8: Ammonia dissociation plant [98]

The key benefits of this type of system are the availability and abundance of the working pair, however, PCMs have seen much more research and recent estimates of the levelised cost of electricity in this sort of plant have not been made [98]. This is likely due to the reported slow reaction rates in ammonia reactors which limits power output as well as the ability to match a varying load [99].

The other ammonia-based system is the 'ammonium hydrogen sulphate system', shown in equation (2.5), first investigated by Wentworth and Chen [100].





However, this reaction is not well studied, and few examples exist outside of the institute of its invention at the Australian National University [101]. This is probably due to the high complexity of the system, resulting from the number of chemicals present, the corrosiveness of the chemicals, and the toxicity of the chemicals. While the theoretical energy density is high (860 kWh/m<sup>3</sup>), other reactions have surpassed the energy density of this one with less toxic and more stable reactants [101]. All of these factors make ammonia-based systems promising, but for now unsuited to domestic applications, largely as a result of the hazards posed by the chemicals, and as a result of the high charging temperature of the reaction. More research into this reaction is necessary.

### 2.2.2 Metal Hydrides

Metallic hydrides have been studied more comprehensively than ammonia-based systems, due to their high efficiency and high energy density across a large turning temperature range, as well as their proven cyclic stability [102], [94]. The three most promising metal hydride reactions are: calcium based, magnesium based, and sodium based [101]. Reactions of these materials along with their associated key data are shown in Table 4.

Table 4: Promising Metallic-Hydrides for TCES

Reaction	Temperature range (°C)	Volumetric energy density (kWh/m <sup>3</sup> )	Ref.
$Ca + H_2 \leftrightarrow CaH_2 + \Delta H$	1100-1400	2050	[94]
$Mg + H_2 \leftrightarrow MgH_2 + \Delta H$	300-480	1110	[103]
$2Na + H_2 \leftrightarrow 2NaH + \Delta H$	600	803	[104]

Despite presenting some of the highest energy densities of any TCES material or reaction known, the use of metallic hydrides present as a TCES material presents the challenge of storing hydrogen at high pressure (50-100 bar), which involves a significant hazard [101]. Metal hydrides also face issues such as sintering of metals at high temperature, and slow reactions. In the context of low temperature TCES for a domestic setting, while the energy density warrants power and a compact system, the very high charging temperature of metallic hydrides together with the need for high pressure hydrogen do not offer a safe, reliable process.

### 2.2.3 Carbonates

The carbonation of materials is an area that has received extensive study, not just within TCES, but also in areas like carbon capture, in order to reduce the GHG emissions and global warming [105]. Specifically, 'Calcium-looping' (CaL) has been investigated as a potential process to utilise the flue gas of some hydrocarbon-based power plant to carbonate limestone (CaCO<sub>3</sub>; Reaction shown in Equation (2.6)) as shown in Figure 9.



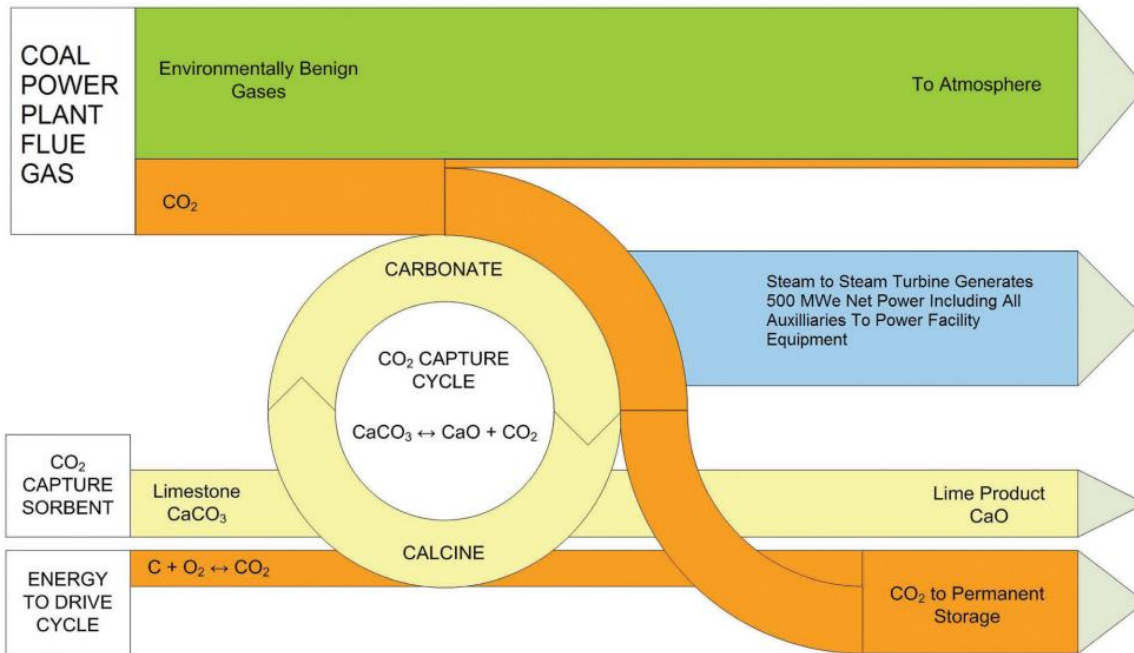


Figure 9: Diagrammatic representation of a calcium looping cycle [106]

This form of carbon capture and storage (CCS) produces highly volumetrically concentrated carbon for only a small fuel cost. CaL TCES also has a comparatively high efficiency and energy density (889 kWh/m<sup>3</sup>) [107]. The chemicals used here are also low cost and are non-toxic [108]. However, like metal-hydrides the CaL process also suffers from sintering and agglomeration. Another drawback is the poor reversibility of the cycle; doping with titanium oxide can improve reversibility as shown by Aihara et al. [109], but the introduction of this high value material inevitably increases the cost of the system.

Another carbonate reaction to receive investigation is the decarbonation of cerussite (PbCO<sub>3</sub>), see Equation (2.7). This process occurs at extremely high temperatures (~1730°C) and is not particularly well researched as a TCES reaction. Kato et al. [110] investigated its potential as a heat pump for very high temperature gas. The study found the reactor to have a specific energy density of 800-900 kJ/kg (~300 kWh/m<sup>3</sup>).



The full potential of carbonation reaction to support TCES remains unclear. Depending on the pair, the materials can provide a clear advantage over ammonia-based systems and metallic hydrides, at a reasonably high energy density. They can likely be applied at the district scale, such as CSP plant, but the high operating temperatures pose a challenge to the development of a domestic setting.

### 2.3 Thermochemical Energy Storage Practical Applications

Due to the relative infancy of the field of TCES, there are few studies that have practically applied the technology, however, there certainly are some. As a result, much of the research on the applications of TCES has been theoretical and model based or has been in selecting the most suitable reaction for an application based on laboratory tests. As mentioned previously, TCES has shown potential in CSP plant



energy storage. This has been reviewed in detail by Prieto et al. [111]. The general conclusions drawn are that no TCES cycle has yet emerged as the best candidate for CSP energy storage, each promising cycle clearly presents its own respective challenges to overcome. Cycles based on the decomposition of sulphuric acid present the issue of highly corrosive sulphur dioxide gas and water which has the potential to seriously damage system components [112]. Cycles based on utilising perovskite membranes have shown promise but still face issues in unknown toxic results that arise from the doping of the perovskite, as well as a lack of prove of the technology outside the laboratory [111]. Prieto et al. drew the conclusion that the most suitable cycle in this application is that based on calcium carbonates i.e., calcium looping [113].

In the case of applying thermochemical energy storage to industrial energy storage applications, emphasis has been put on industrial waste heat recovery [45]. This is especially applicable to lower temperature TCES working pairs as the amount of waste heat generated is typically higher at lower temperature. One of the key benefits of using TCES in this application is its lower cost to transport heat when compared with other methods of waste heat recovery (district heating and transportation of PCM, as shown in Figure 10) [114]. TCES can also be used to upgrade waste heat (increase the temperature) so that it can be used in more industrial processes. T.X. Li et al. [115] proposed a sorption TCES energy upgrade system for recovering waste heat with the advantage of being 10 times more energy dense than its latent and sensible heat storage counterparts. Seeing the potential benefit of TCES in this application, Michel and Clause [116] developed a screening process to assist in the selection of appropriate TCES pairs for application in industrial waste heat recovery. They screened 4290 configurations based on heat transfer, reaction kinetics, and turning temperature to select the three most promising TCES pairs. These pairs are as follows:  $\text{CaCl}_2/\text{Ca}(\text{NO}_3)_2$ ,  $\text{CaCl}_2/\text{SrBr}_2$ , and  $\text{CaCl}_2/\text{K}(\text{OH})$ .

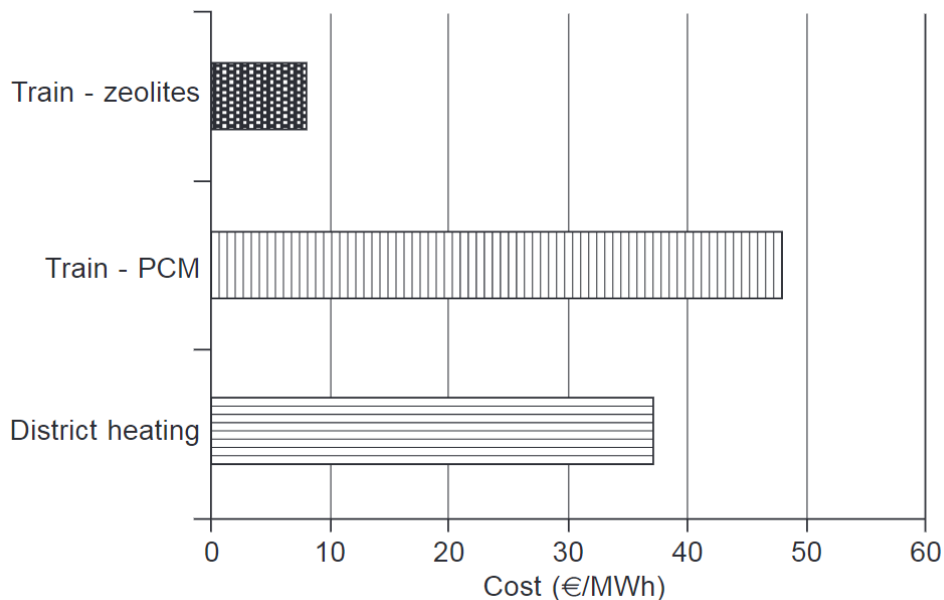


Figure 10: Cost of waste heat recovery by technology, transportation of waste heat and direct use in district heating [117]

TCES has been applied at the domestic scale in research, but yet has not been commercialised. A few notable examples of promising experimental studies in this application exist. The PROMES laboratory is developing a TCES store for operating space heating and cooling, which is charged by a flat plate solar

thermal collector [96]. A 2-year study of this system, which uses  $\text{NH}_3/\text{BaCl}_2$ , as its working pair, showed a global COP of 15 - 23%. The previously discussed research of van Alebeek et al. also demonstrates another example of this application of domestic TCES [60]. This research looked at a system scaled for a single domestic domicile and using Zeolite 13X paired with water as its chemical pair. A 250L system provided 52 kWh of storage capacity and has shown to be highly promising for domestic space heating. Many studies have shown that this application has potential to be commercially successful, however there are still major challenges arising from the relatively high power requirements of some domestic processes, as postulated by Belz et al. [118].

Research in the area of TCES for district heating is showing early signs of potential. Sculler [119] et al. have suggested that the addition of a Zeolite 13X based TCES system would vastly increase the energy utilization of a district heating network. Critoph et al. [120] investigated the use of liquid-gas TCES systems for use in district heating, and evaluated the potential chemical pairs used. The authors identified the chemical pair of  $\text{NaOH}/\text{H}_2\text{O}$  as the best candidate for further study in this application, due to its preferable economic costs, and high heat of vaporisation. Li et al. [121] simulated using  $\text{MgO}/\text{Mg}(\text{OH})_2$  as a reaction for TCES in district heating, and also achieved very promising results demonstrating its effectiveness. 94.6% of the heating demand was able to be met with a system combining TCES and solar heat. Böhm and Lindorfer [122] also performed a techno-economic analysis of TCES in district heating and found that TCES was far less economically effective in districts requiring peak load coverage. Hence the authors concluded that TCES was better suited to grids and districts with a high base load coverage. However overall, the authors suggested that TCES district heating may struggle to compete with pit and borehole thermal energy storage due to lower conversion rates.

## 2.4 Thermochemical Energy Storage Conclusion

Thermochemical energy storage clearly presents a high potential area to solve the issue of energy storage for domestic heat. The key properties of the various TCES media and systems have been given in Table 5. Coupled with a renewable energy source, TCES has the potential to store energy long enough to mitigate the seasonal nature of some of these energy sources. TCES also has the energy density to feasibly store the energy domestically. Sorption TCES seems better suited to domestic energy storage as a result of its discharge and charge (turning) temperature, as well as its proven cycling stability [77]. However, the field of zeolite molecular sieves (which has seen extensive study) could be hampered by low maximum energy density. One of the highest reported volumetric energy densities in this field is  $200 \text{ kWh/m}^3$  [60], which is not much higher than energy densities of more established technologies such as PCM based thermal energy storage [29]. The emerging field of composite TCES materials, which combine a host matrix (often molecular sieves) with a hygroscopic salt can take advantage of the high stability of the host matrix and the high energy density of the salt ( $866.67 \text{ kWh/m}^3$  in the case of magnesium-chloride [55]). Reaction based TCES presents an interesting case, with the highest reported energy densities of any TCES material, but this often comes at the cost of exceedingly high turning temperatures making this field of chemicals largely unsuited to domestic applications. Despite this, some reactions which straddle the line between reactions and sorption TCES cannot be discounted. For example the deliquescence reactions of composite salt based TCES, which have been utilised in combination with sorption TCES to present high energy densities ( $308 \text{ kWh/m}^3$  was reported by J.X. Xu et al. [91]) when compared with other composite TCES. Despite all these highly promising results, there remains one key metric which is regularly reported as low, this is the metric of power output. Even large scale TCES systems with domestic level turning temperatures report a maximum power output of between 1 kW and 2.25 kW [62]–[64]. Clearly, this is far too low.

This has been highlighted as a key issue throughout the literature [11], [62], [63], [98]. Domestic scale TCES systems typically experience poor heat transfer within the TCES system; and thus, power output of the system is low. Li et al. [123] reported a maximum power of 0.15 kW when modelling a composite expanded graphite and LiOH TCES for low grade thermal heat storage. Li et al. [123] proposes that a TCES system be coupled with a standard household heat storage system in order to achieve viability. Van Alebeek et al. [60] tested a 250 litre Zeolite 13X TCES system and found a maximum deliverable power of 4.4 kW, which is the highest reported in literature for this type of TCES system. Considering that typical household processes like a hot shower demands at least 16 kW of water heating, a TCES system alone cannot provide enough power for a typical household. This issue means that a TCES system would need added complexity through some other heat storage which can provide a higher power output than the TCES system.

The literature demonstrates a few key issues that arising in research of TCES materials and systems. Some materials have demonstrated that they can achieve far higher energy densities than traditionally researched TCES materials [55], [91], [124]. Some molecular sieves which have previously been considered good candidates for TCES storage can now be discounted on the basis very low energy storage density especially when compared with the new classes of materials which are emerging. In low temperature applications, pure silica gel and Zeolite based TCES is no longer competitive when compared with composite TCES materials, especially those based on salt-hydrates. Within the composite class of materials, MOF based composites seem very interesting especially due to the huge number of possible materials and combinations of properties that exist [71]. However, while a tremendous amount of research in the field focuses on energy density, there are unanswered questions on how this density can be effectively leveraged into real world applications and needs. New materials offer high energy densities, but their long-term stability and cyclability must be proven, along with the previously mentioned point of power output. In the field of high temperature TCES, which has seen more real-world application, these issues of materials cyclability and limited power outputs have already emerged as key issues [93]. Hot spots which cause material degradation, as well as limited power outputs may be alleviated by certain novel reactor designs. There are also issues such as limited mass transfer leading to slower reaction times, reducing the exergetic efficiency of a system, as well as its power output. Again, solutions for these issues may emerge in reactor design rather than material design. As a result of all of this, the authors suggest that the highest value path of research in TCES would be to look at low temperature TCES reactor design. This is in first part due to the potential success of this research path in high temperature TCES, and in second part due to the lack of investigation currently present in this specific field.

Table 5: Comparison and summary of properties and applications of TCES media and systems \*Data on volumetric energy density is not available

Type	Media/System Type	Volumetric Storage Density (kWh/m <sup>3</sup> )	Temperature Range (°C)	Suitable Applications	Storage	Drawbacks	Ref.
Sorption	Zeolites	136 - 200	25 - 230	<ul style="list-style-type: none"> <li>• District seasonal TES</li> <li>• Domestic Seasonal TES</li> <li>• District heating from Industrial waste heat recovery</li> </ul>		<ul style="list-style-type: none"> <li>• Moderate density</li> </ul>	[59]–[61], [125]
	Silica Gels	31 - 41	130 - 150	<ul style="list-style-type: none"> <li>• District seasonal TES</li> </ul>		<ul style="list-style-type: none"> <li>• Very Low density</li> </ul>	[54], [125], [126]
	Metal-Organic Frameworks	0.17 kWh/kg *	30 - 100	<ul style="list-style-type: none"> <li>• Domestic seasonal TES</li> </ul>		<ul style="list-style-type: none"> <li>• Moderate density</li> <li>• Low level of research</li> </ul>	[71]
	Aluminophosphates	0.13 kWh/kg *	30 - 277	<ul style="list-style-type: none"> <li>• District seasonal TES</li> </ul>		<ul style="list-style-type: none"> <li>• Moderate density</li> <li>• Low level of research</li> </ul>	[79], [80]
	Salt Hydrates	361 - 867	24 - 214	<ul style="list-style-type: none"> <li>• District seasonal TES</li> <li>• District heating from Industrial waste heat recovery</li> <li>• Domestic diurnal TES</li> </ul>		<ul style="list-style-type: none"> <li>• Prone to caking</li> <li>• Poor reaction kinetics</li> </ul>	[55]
	Composites	166 - 308	30 - 250	<ul style="list-style-type: none"> <li>• District seasonal TES</li> <li>• Domestic Seasonal TES</li> <li>• District heating from Industrial waste heat recovery</li> </ul>		<ul style="list-style-type: none"> <li>• Research outside of the laboratory is limited</li> </ul>	[91], [124]

Reaction					
Ammonia Based	< 860	350 - 750	<ul style="list-style-type: none"> <li>• CSP seasonal TES</li> <li>• CSP diurnal TES</li> </ul>	<ul style="list-style-type: none"> <li>• High charge temperature [98], [99]</li> <li>• Low level of research</li> <li>• Safety issues</li> </ul>	
Metal Based	803 - 2050	300 - 1400	<ul style="list-style-type: none"> <li>• CSP seasonal TES</li> <li>• CSP diurnal TES</li> <li>• Combined heat and power energy storage</li> </ul>	<ul style="list-style-type: none"> <li>• High charge temperature [94], [102], [104]</li> </ul>	
Carbonates	300 - 889	500 - 1730	<ul style="list-style-type: none"> <li>• CSP seasonal TES</li> <li>• CSP diurnal TES</li> <li>• Carbon capture &amp; energy storage (CaL)</li> </ul>	<ul style="list-style-type: none"> <li>• Poor reversibility [107],</li> <li>• High charge temperature [108], [110]</li> </ul>	

## 3 Energy Storage in Fluidised Beds

### 3.1 Gas-Solid Fluidisation

Passing a gas with increasing superficial velocity through a bed of powder leads to a linear drop in pressure until a maximum. At this point, the gas velocity is termed the minimum fluidisation velocity, the upwards drag on the solid phase is enough to counter the weight of the powder and form an emulsion or mixture of gas and particles, said to be fluidised. In these conditions the solid phase dilates and behaves as a fluid-like material. A further increase in the gas velocity leads to fluctuations in the pressure drop resulting from specific flow features such as formation of bubbles, that promote the mixing of solid phase. The fluidisation behaviour varies drastically for different materials depending on the balance of drag, gravity and particle-particle cohesive forces. Four major classes are described in the Geldart classification considering the relative effects of the gas and solid densities, and the particle size in drag and weight [127]. As soon as a bed of Geldart B particles is fluidised, an increase in the gas velocity causes gas bubbles to form and rise through the bed promoting the circulation of solids. A bed of a lighter/finer aeratable powder, A, is more susceptible the effect of the particle-particle cohesive forces. In addition to the weight, the bonds established between individual particles must be overcome to turn the bed into a mobile gas-solid emulsion. These forces are more prevalent in a fine powder, and so they cause a Geldart A bed under minimum fluidisation to first expand before reaching a stable bed height (or solid fraction), and bubbling at higher velocities, beyond the minimum bubbling velocity. Not all powders can be fluidised. A bed of even finer/lighter powder becomes too cohesive, C. The prevalence of particle-particle interaction will force the air to create channels and push and break large parts of the bed without forming a homogeneous mixture. Many factors other than size and shape affect the cohesiveness of a powder. Beyond van der Waals forces, capillary and viscous forces bind particles together through the creation of liquid bridges in the presence of a binder (e.g. water), and solid bridges may result from sintering depending on the solids surface properties. In the context of reactive processes such as the ones associated to TCES, particle properties and their evolution through multiple charge and discharge cycles play a crucial role on their fluidisation behaviour. On the other side of the spectrum, the motion of a bed of heavy/large D particles is dominated by gravity and may not sustain bubbling. Instead, a bed of Geldart D particles circulates through spouting, whereby particles are driven upwards by a high-speed channel and accumulate at the side of the chamber forming a long-range recirculation.

When is possible to select the characteristics of a material, gas-solid devices would generally target operation under Geldart A or B to warranty good mixing of the solids. Geldart C particles are very hard or impossible to fluidise without aids such as mechanical vibration, pulsation or specialised designs [128]. Spouted beds can control the circulation of Geldart D powders, but their large size is undesirable for any relative process where one would try to minimise the size of the particles to increase the surface area while still delivering good mixing. The fluidisation behaviour also depends on the applied gas flow rate, see Figure 11. When the gas velocity through a bed of Geldart B or A powder increases, it transitions from a fixed bed to minimum fluidisation conditions with or without expansion before exhibiting bubbling. Bubbling is the optimal regime to maximise heat transfer between the gas and the solid phase. Increasing the gas velocity further increases the size of the bubbles causing more vigorous mixing and establishing a trade-off between the beneficial effects of homogenising the solid phase and increasing the slip velocity and the detrimental effect of proportion of the inlet gas bypassing any contact with the solid phase. Operating at higher and higher velocities, bubbles can grow and coalesce to the point of reaching the

diameter of the chamber, turning the bed into a slugging system. Slugging not only is detrimental to heat and mass transfer, but results in vibration and large pressure fluctuations [129]. Increasing the velocity of the fluid further will lead to the formation of a turbulent bed characterised by a heterogeneous dispersion of bubbles of varying sizing and a large entrainment of powder carried over with the gas downstream. Eventually, at a high gas velocity the entire powder bed can be diluted and carried away through pneumatic transport [130], [131].

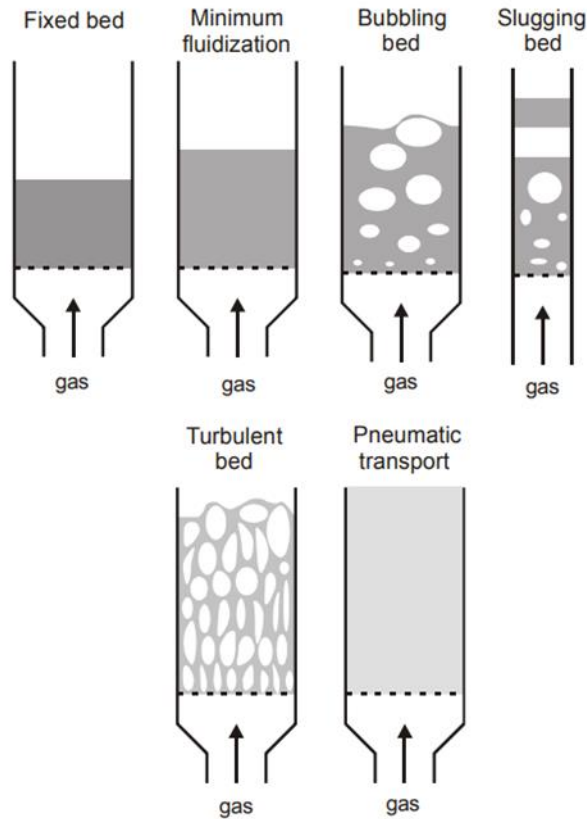


Figure 11: Different fluidised bed regimes [132]

A basic design of a fluidised bed relies on the prediction of the pressure drop and therefore the required minimum fluidisation conditions. Operation above this target gas flow then will be produce the bubbling behaviour and mixing expected in A and B classes. The relation between pressure drop, bed expansion and minimum fluidisation has been studied over many decades. The research by Kozeny and Carman established a first relationship between pressure drop and the fluid and particle properties, later extended by Ergun [133].

$$\frac{(-\Delta p)}{H} = 150 \frac{\mu U (1 - \varepsilon)^2}{d_p^2 \varepsilon^3} + 1.75 \frac{\rho_f U^2 (1 - \varepsilon)}{d_p \varepsilon^3} \quad (3.1)$$

The first and second terms of the Ergun equation accounted for the laminar and turbulent contributions to the pressure loss of a fluid traveling through a packed bed [129]. The minimum fluidisation velocity 'U<sub>mf</sub>' can then be calculated at the point where the pressure drop balances the normal stress created by the bed of powder over the area of the chamber. However, minimum fluidisation is also dependent on

particle properties and the void fraction ' $\varepsilon$ ' achieved at minimum fluidisation depends on the type of powder and the expansion observed. A wide number of empirical correlations are available to predict ' $U_{mf}$ ' of different powders. The general method described by Wen and Yu [134] is perhaps the most widely used. It provides an estimate of ' $U_{mf}$ ' predicting the Reynolds number at incipient fluidisation as a function of the Archimedes number ( $Ar = (\rho_f(\rho_p - \rho_f)gd_p^3)/\mu^2$ ) see Equation (3.2) [134]. Among many others, Baeyens and Geldart [135] provide alternative correlations for particles finer than 100  $\mu\text{m}$ , see Equation (3.3) [129].

$$Re_{mf} = \frac{\rho_f U_{mf} d_p}{\mu} = 33.7(\sqrt{(1 + 3.59 \times 10^{-5} Ar)} - 1) \quad (3.2)$$

$$U_{mf} = \frac{(\rho_p - \rho_f)^{0.934} g^{0.934} d_p^{1.8}}{1110 \mu^{0.87} \rho_f^{0.066}} \quad (3.3)$$

Knowledge of ' $U_{mf}$ ' allows setting a target flow rate, typically well over minimum fluidisation conditions to ensure a vigorous mixing. The expansion of the fluidised bed under those conditions must be accounted for to determine the increase in the height of the bed. The void fraction is often estimated with the Richardson and Zaki relationship that relates the superficial fluid velocity ' $U$ ' to the solid fraction ' $\varepsilon$ ' and the terminal particle velocity ' $U_t$ ', see Equation (3.4) [136].

$$\begin{cases} Re_p \geq 500 & U = U_t \varepsilon^{2.4} & \text{with } U_t = 1.74 \sqrt{\frac{d_p(\rho_p - \rho_f)g}{\rho_f}} \\ Re_p \leq 0.3 & U = U_t \varepsilon^{4.65} & \text{with } U_t = \frac{d_p^2(\rho_p - \rho_f)g}{18\mu} \end{cases} \quad (3.4)$$

A detailed description of the design of gas-solid fluidised bed is available in very well-known literature and beyond the scope of this work. In the context of TCES, the key advantage of a gas-solid fluidised bed stems from the improvement of the rates of heat and mass transfer. Well-known correlations for gas-particle transfer are available in Kunii and Levenspiel [130]. When a bed is designed incorporate heating/cooling elements, correlations must be based in the heat transfer over an immersed surface, such as the Zabrodsky correlation, see Equation (3.5) [137], [138] or the Khan, Richardson, and Shakiri correlation [139], see Equation (3.6), correlations for Geldart B and A powders respectively.

$$h_{max} = 35.8 \frac{k_g^{0.6} \rho_p^{0.2}}{d_p^{0.36}} \quad (3.5)$$

$$Nu_{max} = 0.157 Ar^{0.475} \quad (3.6)$$



The relative area of direct contact between particles and immersed surfaces is relatively low. Thus, fine particles such as Geldart A would typically tend to exhibit the highest bed to surface heat transfer coefficient. Transfer predominately occurs through the convection in the gas-particle interphase, limited by the low conductivity of the fluidising gas. Fine particles present a higher surface area and a thinner thermal layer around them thus maximising the convective heat transfer coefficient. Of course, the convection coefficient also increases with increasing slip velocity, which becomes increasingly available for larger sizes. Note that the increase in velocity leading to vigorous bubbling can improve heat and mass transfer, but also introduces bypassing affecting the efficiency in the usage of the gas, and a potential source of attrition in brittle powders. The formation of finer powder within a bed then leads to a loss of powder carried away with the solids. If this is not a concern, a range of fluidised bed designs can operate at high air velocities as a turbulent fluidised bed by forming a circulating system (circulating fluidised bed) where the material elutriated with the gas flow is collected in a series of cyclones and brought back to the reactor chamber.

A very wide range of fluidisation technology is available to gas-solid operations across manufacturing, energy, environmental sectors, covering almost every type of process, from multiphase reactors to absorbers, dryers, or granulators. The objective of this work is certainly not to review the design strategies of fluidised beds, but to summarise their current range of application in energy systems and highlight certain opportunities. If TCES particles could be sized correctly, there is potential to use TCES systems within a fluidised bed reactor. This has already been extensively taken advantage of in high temperature TCES systems used to store surplus energy in CSP plants [105], [140]–[146].

### 3.2 Fluidised Beds in Sensible and Phase-Change Storage

Fluidised beds have been applied in phase-change material heat storage to improve the storage efficiency and decrease the charging time of Phase Change Materials (PCMs). They have been specifically applied when using micro-encapsulated PCMs, i.e. PCMs imbedded into solid capsule or matrices to reduce corrosion, decomposition, and leakage [29]. Micro-encapsulation, much like composite-TCES, lends itself to the technology of fluidised beds as the granular nature and size of the micro-encapsulated PCMs often aligns with the specific density and particle diameter requirements in a fluidised bed.

Izquierdo-Barrientos et al. [147] performed an experimental investigation of a cylindrical heat storage tank filled with particles operated with a hot air stream to charge, and a cold-water stream circulating inside a helically coiled heat-exchanger immersed within the bed to discharge (this is shown in Figure 12). Both fixed and fluidised bed configurations were studied. A comparison between sand (benchmark) and a granular PCM with latent temperature glide of 40–50°C was carried out. Rubitherm-GR50 was used with both finer (540 micron) or coarser (1640 micron) particle size. The effect of the coil pitch has been parametrically analysed to evaluate the effect on the heat transfer performance. Overall, higher heat transfer coefficients are achieved with greater pitch, as bed particles and the heat exchange surface have better thermal contact when the particles are fluidised. An overall heat transfer coefficient ( $U$ ) of up to 320 W/m<sup>2</sup>K in the discharge phase (i.e., with water being heated up from bed) was observed; this is an enhancement when compared to the 280 W/m<sup>2</sup>K achieved for sand when using fluidised beds. Interestingly, when testing fixed beds, sand achieved better overall heat transfer coefficient compared to PCM (up to 140W/m<sup>2</sup>K versus 120 W/m<sup>2</sup>K). The study also indicated that in a tank heated by solar air collectors, that the charging process should be done in fixed-bed conditions to maintain the bed stratification. Further, the study suggested that the discharge process be done under fluidised conditions

to increase the heat transfer rates. Izquierdo-Barrientos et al. [148], [149] followed up on this work by proposing a numerical model for the heat transfer coefficient in packed beds, validated with experiments for both sand and PCM. The potential benefit of PCM could be limited because there is no renovation of the particles touching the heat transfer surface, which are the ones where the PCM is in liquid form. The experimental validation of the model follows this study into the numerical model of the heat transfer coefficients [150]. This study experimentally investigates the variation of heat transfer coefficients from fixed to fluidised beds with PCMs. Fluidised beds lead to three times higher heat transfer coefficient compared to fixed beds [150]. This is mainly due to renewal of PCM particles when fluidised. In the fixed bed there is no ‘renovation’ of particles, consequently only a small percentage of particles are able to change phase.

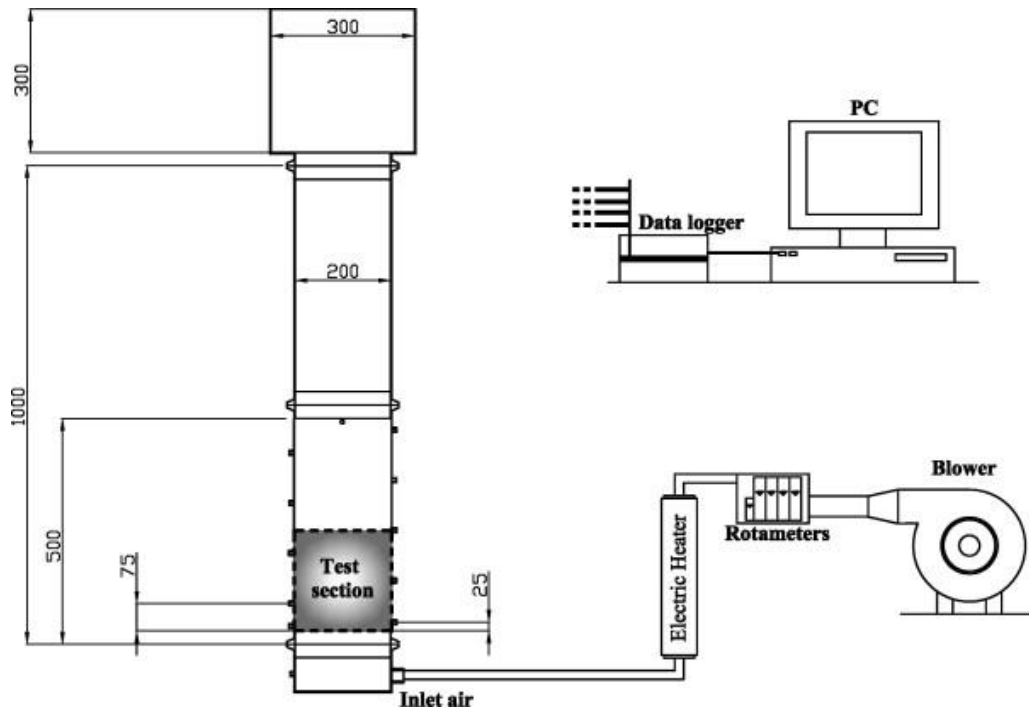


Figure 12: Schematic representation of the experimental apparatus (Dimensions in mm) described by Izquierdo-Barrientos et al. [147]

Almendros-Ibáñez et al. [44] reviewed energy storage in packed and fluidised beds. The review concluded that the main advantage of packed beds is their ability to generate thermal stratification; this increases the 2<sup>nd</sup> law efficiency (exergetic efficiency) of the solar collectors in low-temperature sensible energy storage systems. It also has the benefit of augmenting the exergy content of the bed. The review asserts the following: “To the author’s knowledge, there is no relevant research on the use of fluidised bed technology for thermochemical energy storage in the low-temperature range (below 150 °C).” Thus, more investigation is certainly required in order to ascertain the effectiveness of fluidised beds in the context of domestic TCES.

Izquierdo-Barrientos et al. [151] tested direct contact fluidised beds (no heat pipes) and their performance in sensible heat storage (sand), and a micro-encapsulated PCM (Rubitherm-GR50 of different coarseness’s), and tested and compared these results with packed beds. The system was cylindrical, and

air based. The sand particles, and the finer PCM were both Geldart class A particles. The coarser PCM was on the transition line between Geldart class A and class B. Overall, PCMs guarantee higher charging efficiencies for both fixed and fluidised beds compared to sand; also, evidence shows that higher air velocity and lower bed height increase charging rate but decrease efficiency. Due to the composite nature of the PCM, the latent heat is reduced to a maximum of 54 kJ/kg compared to typical values of pure paraffins (160-190 kJ/kg). Importantly, the tests show that PCM suffers attrition during fluidisation, however no PCM leakage was observed during 75 h of operation with 15 cycles. This paper demonstrates that attrition could present an issue when applying fluidised beds to thermal energy storage applications. While the authors demonstrated the systems stability for 15 cycles, a diurnal energy storage system would need to last for many more cycles than this.

Pitie et al. [152] was the first to suggest the use of coated PCM particles in a circulating fluidised bed. They investigated the potential of this concept through modelling and experimentally testing a system which fluidised particles  $<400\ \mu\text{m}$ . Their study focused on maximising the heat transfer coefficient from the wall of the heat exchanger to the bed. Heat transfer coefficients of 60 to 350 W/m<sup>2</sup>K were measured. Gomez-Garcia et al. [153] built on this work and designed and parametrically studied a sensible particle based heat storage plant which utilised circulating fluidised beds. This heat storage plant was for a heliostat CSP tower which undergoes extremely high temperatures. The authors claim to be first to develop a modelling of a novel sensible heat particle fluidised bed heat-exchange multistage system to overcome the typical limits of state-of-the-art molten salts receiver, i.e., high costs, low max temperature (565°C), and low power cycle max temperature of 220°C (i.e., solidification temperature of the molten salts, PCM). Due to the high temperatures, solid particles are used instead of a fluid such as thermal oils or molten salts. These fluids can face many issues at these high temperatures [11]. The plant used multiple fluidised beds, and a Rankine steam generator to convert the heat energy stored in the particles into electricity. In their design, cold particles emerge from the cold storage and are heated in the standard CSP solar receiver and then stored in the hot storage. Importantly, particles are moved in counterflow current in several in-series heat-exchange tanks. A thermal and global efficiency of 99.3% and 49.7% were found respectively. A maximum temperature difference of 387°C between the plant outlet and inlet was also found, which is 117°C higher than the maximum temperature difference in current molten-salt storage tanks in solar towers [153]. This study presents a fluidised bed reactor with very high thermal efficiency, and also a significant temperature lift between the inlet and the outlet of the reactor. One potential issue of fluidised beds in thermal energy storage that has been discussed is the exergy losses involved with significantly increasing the fluid flow rate through energy storage system, in order to achieve the fluidisation. Also, the lack of thermal stratification will reduce the exergy content of the bed as shown by Rosen [154]. This high temperature lift shown by Gomez-Garcia et al. [153], suggests that fluidisation may not detrimentally effect the quality of the heat produced by a thermal energy storage system.

Beemkumar et al. [155] analysed a fluidised bed and fixed bed storage system with different PCM (D-Mannitol) encapsulation materials (aluminium, brass, and copper). Capsules are of orbicular shape with 4 inches diameter and 2 mm thickness. Therminol-66 is used as a heat transfer fluid (HTF). From a techno-economic analysis, aluminium in fluidised bed has the lowest cost per kWh compared to copper and brass (33.33 % and 22.22 % less than copper and brass respectively). However, copper guarantees the highest heating rate as the mean heating rate of aluminium encapsulated PCM in both fixed and fluidised beds is about 12% less than copper while 10% higher than brass. One interesting point in this study was that while the charging power for copper PCM was significantly increased in from the packed bed to the fluidised

bed (3.65 kW to 5.98 kW), the discharge power only increased marginally (2.73 kW to 2.81 kW). The authors did not offer an explanation for this, but it potential casts doubt on the suitability of fluidised beds in PCM heat storage, and certainly would merit further investigation.

A two part study was conducted by Wünsch et al. [156] and Sulzgruber et al. [157] working on fluidisation-based particle thermal energy storage (FP-TES). The authors have designed a sensible heat store which uses a fluidisation-based heat exchanger. The first study was numerically based, and the second study experimentally based. With the help of a Computational Particle Fluid Dynamics (CPFD) model, the authors propose a parametric analysis on the geometrical and fluidic parameters, leading to the optimisation of the system by means of rotational symmetric hoppers with additional baffles in the internal heat exchanger and internal pipes. The in this study, authors focussed on the design of the bed and studied the areas where thermal insulation was important and did not investigate the thermal performance of the bed. The experimentally based second part to the study provided several interesting results. Scaling up the experimental results to a bed heights and diameters of 2m and 3.5m respectively, the bed was able to produce an extremely high-power output of 545-2406 kW when using Corundum powder as the storage material, and 296-1308 kW when using Quartz sand. These results were for discharge times of between 2.3 and 10.3 hours. The authors clearly intend for this technology to be used at the industrial scale with the bed sizing being unsuitable for domestic applications. However, the results do suggest the potentially large power outputs brought about by applying fluidisation technology to the sensible thermal energy storage.

### 3.3 Fluidised Beds in Thermochemical Energy Storage

Several of the characteristics of fluidised beds are potentially very advantageous in TCES, Many authors have attempted to take advantage of the higher heat and mass transfer in a fluidised bed in order to improve the energy density of heat storage materials, which is especially important because mass transfer is often the main limitation in thermochemical energy storage beds [158]. Fluidisation has the potential to solve the problem of limited mass transfer in TCES, as well as potentially decrease charge and discharge times.

Concepts like moving beds, occupy the space between fluidised beds and packed beds. In a moving bed the bed of particles is moved in some way but not fluidised; this promotes heat transfer and temperature uniformity within the bed. Farcot et al. [159] experimentally investigated the potential of downward moving beds using salt hydrates as the storage material. It was found that the moving bed achieved temperature uniformity throughout once reaching its steady state which occurred about 45 mins into the cycle (cycle time of 10 hours). The study also demonstrated the feasibility of the system; however, the bed had many flow issues due to agglomeration of the salt. Recently, research in moving bed reactors has often been in the stabilisation of the size of the materials. Xia et al. [160] used carboxymethyl cellulose sodium and vermiculite to achieve this stabilisation, and increased the volumetric storage density by approximately 124%. This clearly demonstrates that active bed movement is able to increase the storage density in the case of moving beds.

Two broad categories of fluidised beds have been applied in thermal energy storage. These are: Bubbling fluidised beds (BFBs) and circulating fluidised beds (CFBs). BFBs are 'traditional beds' with a fixed chamber of particles. CFBs are beds which circulate the particles in and out of the bed, without a clear and recognised freeboard area [161]. A diagram demonstrating the differences in the two bed types in the context of combustion processes (the beds operate in the same way in the context of TCES, with the key

difference being the lack of a combustion process) is shown in Figure 13. CFBs can typically be applied where the size of the heat storage is very large and can offer high heat outputs. This comes at the cost of increased complexity, and particle attrition and abrasion [162]. BFBs are less complex and are more suited to smaller scale storage. Due to the fact that fluidised beds for thermochemical storage have mostly been applied for high temperature large scale CSP; CFBs have seen more investigation in this area. BFBs and CFBs have been compared extensively in the field of combustion and gasification in fluidised beds, and the broad conclusions drawn are that CFBs offer better mixing, and thermal throughput (1200 - 1600 kW/m<sup>2</sup> in BFBs compared with 5000 - 7000 kW/m<sup>2</sup> in CFBs), but this comes at the cost have higher investment for a CFB system [163]–[165].

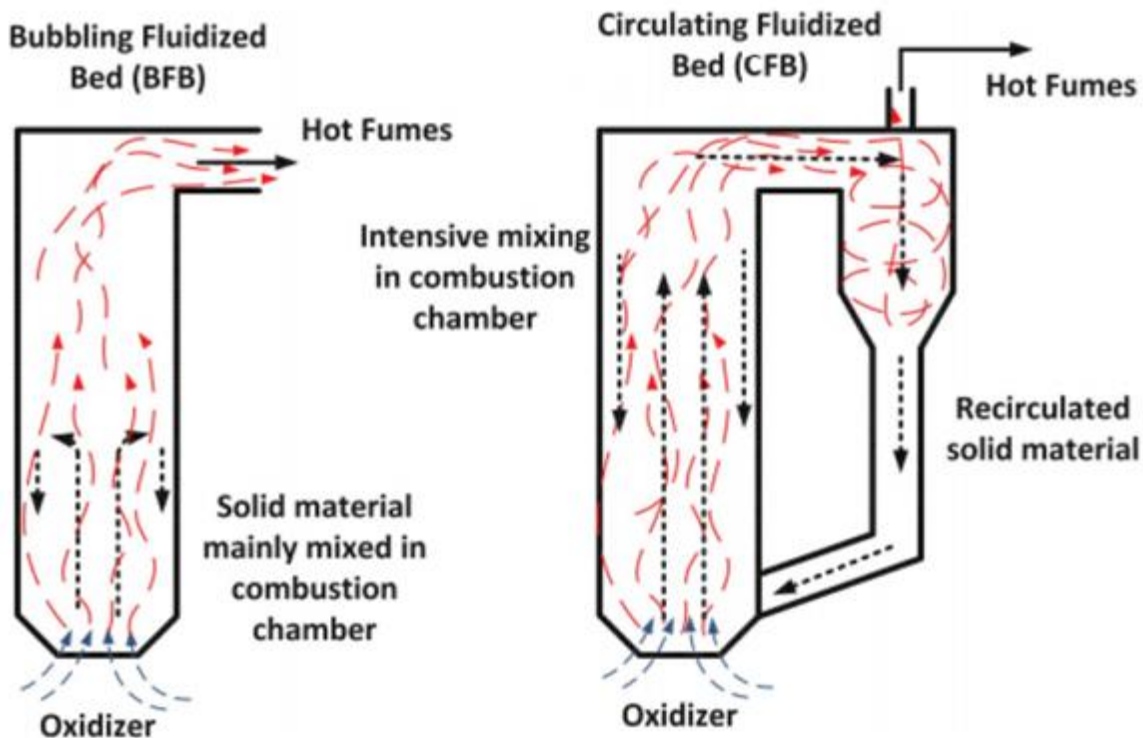


Figure 13: Diagram demonstrating a BFB and CFB in the context of fluidised bed combustion [166]

Fluidised beds significantly increase mass and heat transfer between the fluid and particulate [132]. This has a direct potential to increase the power output of TCES. The higher heat and mass transfer associated could allow a TCES system to function as a standalone storage system to provide heat for relatively high-power demand domestic heat requirements.

### 3.3.1 Bubbling Fluidised beds

Bubbling fluidised beds were initially proposed as a method for improving the heat and mass transfer capabilities of thermochemical energy storage devices by Darkwa et al. [167]. Their model assumed that the system would be non-isothermal due to the rapid reaction process, that the fluid velocity is constant, and that the reactor is insulated and under adiabatic conditions. An axial dispersion model is used to calculate the mass balance, and the calculations were made in the one-dimensional mode of FEMLAB. Calcium Oxide was the adsorbent modelled. Darkwa et al. [167] demonstrated that fluidisation offered

enhanced adsorption capacity (although this appeared to be as a result of a longer residence time) and heat transfer rate compared to fixed beds.

To the knowledge of the authors only two studies exist investigating sorption based TCES in FBRs. These are the studies performed by Darkwa et al. [167] and Bardy et al. [43]. Clearly, research in the application of fluidised beds to TCES storage has been focused on reaction-based systems. The hydration of calcium-oxide has attracted interest due to the non-toxicity and the low capital associated with the material [94]. Pardo et al. [144] and Criado et al. [168] investigated the performance of BFBs and CFBs. The chemical loop investigated was the reaction of calcium oxide and water to produce calcium hydroxide. The equilibrium temperature at 1 bar of water partial pressure was 505°C, and so clearly this reaction is best suited to high temperature CSP [169]. Criado et al. [168] experimentally verified a model of the process for CSP however found a much slowed reaction rate due to the CaO experiencing very high calcination temperatures during its production from limestone (used to give the sample material mechanical strength). This is due to a decrease in free surface area in CaO at high calcination temperatures, the authors did not attempt to investigate the mechanism of this change in reactivity. Sunku Prasad et al. [94] recommended that carbon dioxide be removed from the system to mitigate this, as they suggested that the presence of CO<sub>2</sub> was reducing the reversibility of the reaction. Pardo et al. [144] used calcium-oxide powder (4 µm), and so needed the majority of the bed to be comprised of ETF particles, made of inert aluminium-oxide, in order to achieve a good fluidisation, as in Alavi and Caussat [170]. The aluminium-oxide ETF produced an inertial effect which assisted the fluidisation of the powder and negated cracking and channelling effects; however, the addition of these inert particles decreases the volume available for reactive material. Despite this, they achieved an energy density of 156 kWh/m<sup>3</sup> for the system over 50 cycles. Both agreed that calcium-oxide in a BFB was highly promising as a storage technique for CSP,

The decarbonisation reaction of calcium carbonates was one of the first materials investigated in a fluidised bed as a storage medium, when Badie et al. [171] tested their efficacy and found the fluidised bed to have a better global efficiency and thermal efficiency than rotary kilns (moving bed reactor). However, while a few authors have continued this research in the form of CFBs, simple BFBs have not been investigated further in their application to the decarbonisation of calcium carbonates. This is perhaps due to the very high temperature range (972-1273°C [94]) compared to other forms of TCES, meaning that large very high CSP is the only feasible solar technology which can be coupled with this reaction, and as previously discussed CSP has seen significant investigation in combination with CFBs. So while this reaction has demonstrated that FBRs offer an efficiency improvement over rotary kilns (a form of moving bed), there is a need to understand if this improvement translates to low temperature domestic TCES

Clark et al. [172] reviewed salt hydrates as a TCES material and considered their application in BFBs. The authors recommended BFBs as a technology with the potential to improve mixing in salt hydrate based TCES through increased heat and mass transfer rates but found no investigations of this in literature. They concluded that the feasibility of fluidised beds in salt hydrate based TCES needed to be proven experimentally and via modelling for these reactors. Salt hydrates have a low turning temperature range (From 24 – 214 °C [55]), and as such would be suitable to be applied in domestic TCES.

Ströhle et al. [145] investigated the oxidation of manganese oxide as a TCES reaction. A continuous packed bed was compared with a BFB. The authors demonstrated that the conversion rate was significantly higher in the BFB than the in the packed bed. This was due to only 14% of the particles in the packed bed becoming reacted, while 95% of the material in the BFB reacting. However, the authors believed that the

value of 14% could be somewhat increased through better optimisation, while asserting that in this setting a packed bed could not allow for complete chemical conversion.

Pardo et al. [144], Criado et al. [168], and Badie et al. [171] all achieved promising results, proving the concept of BFBs in TCES, showing cyclic stability (as far as 50 cycles). Pardo et al. [144] and Criado et al. [168] both suggested that further studies were needed to investigate these reactions when applied to CFBs. This is because CFBs are better suited to larger scales (due to the fact that the amount of material that can be reacted is not limited by the size of the bed) it follows that CSP is better suited to CFBs. However, no authors have considered the benefit of the simpler BFB system when it comes to smaller scale storage and generation, for example at the domestic level where generation and storage are smaller. Clearly, BFBs have the potential to be applied here.

### 3.3.2 Circulating fluidised beds

Zondag et al. [173], [174] tested a continuous fluidised bed for thermochemical storage. The reaction studied was the hydration of anhydrous magnesium sulphate salt into its heptahydrate (Epsom salt). The study compared a CFB with an Archimedes screw based 'extruder reactor' and a gravity driven bulk flow reactor. They found that in the CFB, the hydration and dehydration reaction would crack the particles, and the fluidisation would break them apart into a very fine powder. This very fine salt powder would not fluidise properly. This is due to the fact that most fine powders fall into Geldart C classing, and thus will experience serious agglomeration and cohesiveness preventing fluidisation.

Following on from previous work using a BFB, Criado et al. [142] first designed a CFB for the application of thermochemical energy storage. The TCES material used was calcium oxide with the reaction to calcium hydroxide being the storage loop (hydration and dehydration). It was assumed that this CFB would operate similarly to existing CFBs not used for TCES, for example in a CFB combustor. This work was continued by Rougé et al. [143] who produced the first experimental results for this reactor and validated the previously developed model and design. The reactor operated with two separate beds, one for the hydration, and one for the dehydration reaction. This can be seen in Figure 14, this type of reactor would have the advantage of being able to charge and discharge concurrently. The authors verified that this pilot plant functioned, it produced 20 kW of power continuously at a temperature from 400 to 540°C [141]. Wuerth et al. developed a small scale (5 kg/h of storage particles) pilot CFB TCES, also utilising the hydration and dehydration of calcium-oxide as the storage loop [175]. The aim was to prove the concept, however, to date results and data from the reactor have not yet been published.



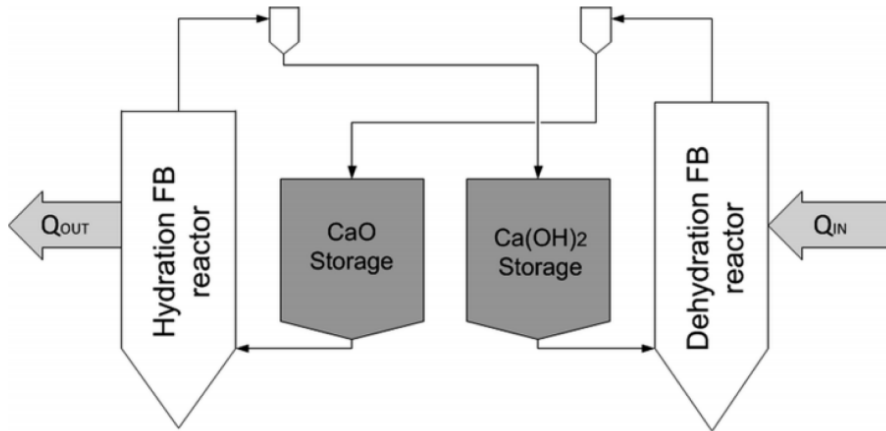


Figure 14: Double reactor CFB-TCES [143]

Flegkas et al. [176], [177] developed a model for a solid-gas thermochemical energy storage system using the hydration and dehydration of magnesium oxide as the storage loop and analysed the profitability of this system. A significant proportion of the heat input into the system (37%) was required just to heat the particles from ambient temperature to their reaction temperature. Due to this, it was suggested that particles entering the bed were preheated by particles exiting the bed. The results highlighted a key issue with TCES, which is that heat can only be released at a much lower temperature than the temperature it is stored at. In the assessment of profitability, the authors assumed the system be installed as a waste heat recovery and storage device. The results suggested that it was uneconomical to install this system where less than 5.2 MW of waste heat were available. These findings clearly point to the likelihood that it is inefficient and uneconomical to use CFBs for small scale energy storage, like that required by singular domiciles.

Like with BFBs, the decarbonisation of calcium carbonates (calcium looping) has been investigated as a storage reaction in CFBs. Chacartegui et al. [107] and Tregambi et al. [178] investigated this concept, with Chacartegui et al. [107] creating a model of the process and Tregambi et al. [178] experimentally simulating the process. The process model estimated that a thermal efficiency of 40-46% is realistically achievable in a CSP plant. This efficiency is significantly higher than traditional Rankine cycle based CSP storage. The experimental simulation of a calcium looping storage system driven by CSP proved the concept, however, the thermal efficiency in the system decreased as the number of cycles progressed. This is likely due to the sintering of the particles at the extreme high temperatures in the calcium looping process. Yan et al. [105] reviewed calcium looping as a storage reaction, and concluded that “(calcium looping) processes are feasible to store solar energy in thermochemical form at high temperature, for diurnal usage, balancing out day-night solar availability”. Also concluding that fluidised beds required further research to investigate their potential to improve heat and mass transfer.

### 3.4 Fluidised Bed Reactors Conclusion

Fluidised beds have seen investigation and application in all three of the major categories of thermal energy storage. They have been shown to produce: improved heat transfer (as much a three times higher), improved cycle stability, and very high-power outputs in sensible and PCM based energy storage technologies [147], [151], [156], [157]. They have also shown to produce a clear improvement in power output over packed beds for under the same conditions [151], although this has not been universal as in



Beemkumar et al. [155]; while maintaining high efficiency [152], [153]. Fluidised beds have been applied to PCMs with the goal of reducing corrosion, decomposition, and material leakage; however fluidised beds have been shown to introduce some attrition on the PCM material [151]. With the key reported downside of fluidised beds being the loss of exergy resulting from the lack of thermal stratification [154]. Nonetheless, fluidised beds have shown promise in thermal energy storage and warrant further investigation into their potential benefits. Overall, it is clear from the literature that FBRs need further research in the context of TCES with very little literature investigating FBRs in domestic TCES [43], [167]. Significant success has been reported in the use of FBRs in high temperature TCES for use in CSP plants [107], [144], [168], [170], [178], as well as in the storage of industrial waste heat [176], [177]. With FBRs improving heat and mass transfer (i.e. power output), as well as temperature homogeneity which is important in avoiding hot spots which can degrade the TCES material [93], [159]. FBRs have even been shown to increase efficiency over traditional processes in some cases [178]. BFBs have seen significant investigation, with many authors suggesting that the next step is to test TCES using CFBs. However, it is not clear which bed type would be best suited to domestic TCES. For now, only BFBs (likely as a result of their simplicity and lower pumping costs over CFBs) have been investigated in the context domestic TCES, and even these investigations still leave many questions unanswered.

The key differences between how fluidised beds have been applied in each case are as follows: In sensible energy storage FBRs have primarily been applied with the goal of improving heat transfer. In PCM energy storage, fluidised beds improve heat transfer, but also have the benefit of potentially reducing material corrosion and decomposition. The application of fluidised beds in TCES differs slightly from the previous two energy storage methods. In this case FBRs have been applied primarily to increase reaction kinetics and thus increase power output, however this application has been more or less confined to high temperature TCES.

## 4 Conclusions

Clearly there is a pressing need to decarbonise heat to avoid a climate catastrophe brought about by anthropomorphic global warming. A large proportion of greenhouse gases originate from heating and without effective energy storage, renewable energy will struggle to meet our global need for heat. The current zeitgeist of how to achieve this goal of decarbonising heat is through electrification, and the scaling up of national grids. However, our electrical generation capacity is not equipped to handle this scaling up of demand, and electrical heating is not feasible for many homes in the first place [179]. Thermochemical energy storage, in conjunction with renewable heat generation technologies such as solar thermal, geothermal, and biomass has been well studied as a solution to the issue of domestic heat. However, the most promising and highest potential renewable energy source in this context, solar thermal heat, poses another problem; the problem of interseasonality and the mismatch between supply and demand between the summer months and the winter months. As the only form of energy storage with a theoretically limitless storage time, this is where thermochemical energy storage can enable solar, and other renewable resources to supply 100% of domestic heat needs.

Thermochemical energy storage is on the cusp of domestic application, and storage mediums such as molecular sieves have shown to be an excellent candidate. Reaction based thermochemical pairs have also shown to be highly effective in high temperature energy storage applications, especially in CSP. They also present the highest known energy densities of any TCES materials. Despite these favourable characteristics, the high toxicity, economic cost, turning temperatures, and volatility of these chemicals

often rule them out for the domestic market. The relatively new field of materials known as composite materials (which combine molecular sieves with hygroscopic salts in order to significantly increase energy density), presents the best of both worlds with regards to energy density, and domestic suitability.

A domestic setting requires a high energy density to have a compact system but is subject to specific constraints. Some of them are defined by the selection of the material: a domestic setting needs non-toxic materials, ideally for an open system hence using water and/or a humidifier, low pressure systems and low-medium temperature processes. This prevents using the high energy reactions discussed, which require high temperatures for charging, so the best suited candidates are sorption systems. Others are defined by the design of the reactor. In a batch system like a TCES, to maintain a long lifespan and cycle stability one must guarantee full conversion, no loss, sintering, or deactivation of the material. This means ensuring that there are no parallel reactions by operating the system homogeneously at the optimal conditions. Power is controlled by the rate of reaction. It can be limited by the reaction's kinetics, but it can also be affected by heat and mass transfer limitations, in other words, how rapid is the delivery of heat and reactants to the solid phase. Limitations can be external (transport of heat of reactants between the continuous to the solid phase) or internal (transport of heat of reactants within each particle). The physical properties of the materials, such as particle size and porosity delimit the internal resistance, but external transport is governed by the design of the reactor and the resulting contact pattern between gas and solid phases. Heat and mass transfer rates depend on the overall circulation, and the slip velocity between both phases. All these design parameters interplay to determine the final discharging and charging power profile.

When looking to maximise power, one tries to accelerate the reaction kinetics and minimise any limitations to heat and mass transfer. Industrial settings can do the former by operating at very high temperatures and/or pressures, but this is not acceptable for a domestic setting. The latter can be achieved with an appropriate design of the reactor. Fixed beds are well suited to deliver high conversion and selectivity but cannot deliver/dissipate heat quickly in highly exothermic/endothermic reactions. This leads to inhomogeneous temperature and concentration fields that reduce the efficiency of the system and are detrimental to the power. This can be addressed by mixing the solids in a moving or a fluidised bed. Different designs and operation regimes are variable depending on the characteristics of the solids involved and their fluidisation behaviour. In these designs, the slip velocity can be increased substantially removing the limitations to heat and mass transfer and maximising the charging and discharging rate. However, vigorous mixing of the solids is likely to lead to attrition and a loss of fine particles being carried by the gas out of the reactor. Therefore, one must strike a balance between the high conversion and selectivity of a fixed bed, and the better homogeneity of a fluidised system. The hydrodynamics of gas-solid systems is very complex, but a range of designs of operating gas-solid fluidised beds is available covering the different behaviour of powders varying in size and density and spanning over a broad range of gas-solid slip velocities.

TCES in an industrial context is already transitioning to the use of gas-solid fluidised beds to maximise power, but no similar applications have been reported for low temperature domestic systems. Domestic TCES needs a particular quick charge and discharge response over a well-defined range of temperatures. While it can be tuned with the material, one cannot drive a fast kinetics increasing temperature and pressure. Therefore, it is particularly important to explore how the use of moving and fluidised beds of materials is suited for TCES can maximise the power of any given material pair, and whether the benefits observed at large scale operation can translate into an economical application at a domestic scale

provided the need for additional instrumentation and a more complex set up than a traditional small scale fixed bed.

Fluidised bed reactors have been studied extensively in high temperature reaction based TCES, as well as in sensible, and PCM based energy storage. These FBRs have been demonstrated to increase the heat and mass transfer in the energy storage medium, consequently increasing the charge and discharge times of the thermal energy store. In reviews of the field, many authors have pointed out the apparent lack of study into the efficacy of FBRs applied to low temperature TCES, suited to domestic applications. Despite this, FBRs have the potential to significantly increase the reaction kinetics of domestic TCES system and solve the issue of low power outputs. It should be noted, however, that FBRs will likely also pose new problems such as increased system complexity, TCES material attrition and degradation, and reduced exergy content. However, these questions have not been answered. In light of this, the authors suggest that the literature points towards the need for further study in domestically applied TCES-FBR systems, specifically in their interaction with the domestically suited area of composite-based TCES. Research in this area could unlock the potential of TCES enable a future where all heat is supplied from renewable energy resources, effectively decarbonising heat to the fullest degree.

## Conflict of Interest

The authors declared that there is no conflict of interest

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