

Salts Hydrates and Composites

Subjects: Chemistry, Applied | Others | Engineering, Environmental

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Salt hydrates are alloys of salts and water. Salt hydrates display high theoretical energy densities, which are promising materials in thermal energy storage (TES).

Keywords: sorption ; heat storage ; thermo-chemical ; energy ; adsorbent materials ; salts ; composite

1. Overview

To improve the proficiency of energy systems in addition to increasing the usage of renewable energies, thermal energy storage (TES) is a strategic path. The present literature review reports an overview of the recent advancements in the utilization of salt hydrates (single or binary mixtures) and composites as sorbents for sorption heat storage. Starting by introducing various heat storage systems, the operating concept of the adsorption TES was clarified and contrasted to other technologies. Consequently, a deep examination and crucial problems related to the different types of salt hydrates and adsorbents were performed. Recent advances in the composite materials used in sorption heat storage were also reviewed and compared. A deep discussion related to safety, price, availability, and hydrothermal stability issues is reported. Salt hydrates display high theoretical energy densities, which are promising materials in TES. However, they show a number of drawbacks for use in the basic state including low temperature overhydration and deliquescence (e.g., MgCl_2), high temperature degradation, sluggish kinetics leading to a low temperature rise (e.g., MgSO_4), corrosiveness and toxicity (e.g., Na_2S), and low mass transport due to the material macrostructure. The biggest advantage of adsorption materials is that they are more hydrothermally stable. However, since adsorption is the most common sorption phenomenon, such materials have a lower energy content. Furthermore, when compared to salt hydrates, they have higher prices per mass, which reduces their appeal even further when combined with lower energy densities. Economies of scale and the optimization of manufacturing processes may help cut costs. Among the zeolites, Zeolite 13X is among the most promising. Temperature lifts of 35–45 °C were reached in lab-scale reactors and micro-scale experiments under the device operating settings. Although the key disadvantage is an excessively high desorption temperature, which is problematic to attain using heat sources, for instance, solar thermal collectors. To increase the energy densities and enhance the stability of adsorbents, composite materials have been examined to ameliorate the stability and to achieve suitable energy densities. Based on the reviewed materials, MgSO_4 has been identified as the most promising salt; it presents a higher energy density compared to other salts and can be impregnated in a porous matrix to prepare composites in order to overcome the drawbacks connected to its use as pure salt. However, due to pore volume reduction, potential deliquescence and salt leakage from the composite as well as degradation, issues with heat and mass transport can still exist. In addition, to increase the kinetics, stability, and energy density, the use of binary salt deposited in a porous matrix is suitable. Nevertheless, this solution should take into account the deliquescence, safety, and cost of the selected salts. Therefore, binary systems can be the solution to design innovative materials with predetermined sorption properties adapted to particular sorption heat storage cycles. Finally, working condition, desorption temperature, material costs, lifetime, and reparation, among others, are the essential point for commercial competitiveness. High material costs and desorption temperatures, combined with lower energy densities under normal device operating conditions, decrease their market attractiveness. As a result, the introduction of performance metrics within the scientific community and the use of economic features on a material scale are suggested.

2. Background

From 2005 to 2030, global energy demand is projected to increase by 50% due to population growth and economic development ^[1]. Energy policy production is now at a crossroads due to decreasing fossil fuel supplies, growing energy demand, and rising greenhouse gas emissions ^[2]. The current energy policy aims to decarbonize the energy system by switching to alternative energy sources, developing new energy production technologies, and increasing energy efficiency ^{[3][4][5][6]}. One of the aims of the Paris Agreement is to migrate entirely away from fossil fuels and toward renewable energy

sources. However, the world's renewable energy potential has yet to be fully realized; only 23% of these energy sources have been used [2]. This opens up a lot of space for strengthening and innovating clean energy policies.

Fossil fuels release greenhouse gases (for instance, CO₂, NO_x, and others), which are damaging the atmosphere. The U.S. Energy Information Administration's Annual Energy Outlook (AEO) report forecasted that by the end of 2020, energy generated from renewable energy sources such as solar, wind, and geothermal will rise to 20 percent. The key problem related to solar and wind energy is their intermittent nature and the lack of ability to generate energy 24 h a day. Consequently, renewable energy storage technologies (REST) that allow for a stable supply chain of energy are crucially required.

There are different approaches to storing energy, comprising the following: electrical energy storage (EES), mechanical energy storage (MES), chemical energy storage (CES), and thermal energy storage (TES) [2][9]. For instance, about 39% of the total energy is used by residential and industrial buildings in the United States; the majority of this energy is used for cooling and heating applications [10]. Batteries are the most popular electricity storage technology, but TES may be the ideal choice when dealing with heating and cooling [2][11][12]. TES devices store energy extracted from the sun, helping to minimize the costs, improve demand-side control with an overall performance improvement, provide improved reliability, and diminish the carbon footprint. District heating/cooling, seasonal storage for commercial and private buildings heating, time-shifting of energy demands, and waste heat recovery are the main applications of TES. Systems designed for TES-based heating or cooling applications have the promising economic advantage of minimizing the cost of capital and maintenance that can satisfy average demand, and not just peak and cycling requirements.

Solar energy, by its nature, is intermittent (day/night), random (thunderstorms and cloud passages), diluted, and delayed on daily or seasonal energy demand. Moreover, its exploitation requires the deployment of high-performance storage systems. In contrast, thermal energy storage technology has reached maturity, which makes it ready to be harnessed for the efficient use of renewable energies. To store energy in the form of heat, there are three basic principles: sensible heat storage (SHS), latent heat (LHS), and thermochemical storage (TCES) [13]. The importance of thermal energy storage compared to other existing technologies is illustrated in [Figure 1](#) [14]. It shows that thermal energy storage allows for the management of high power over long periods of time.

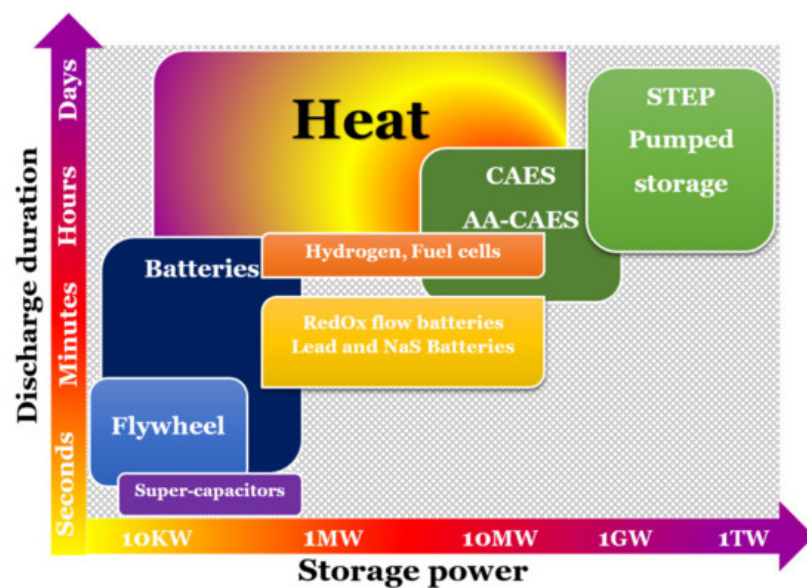


Figure 1. Different storage technologies depending on their storage power and discharge time.

Energy storage is about saving a quantity of the stored energy for later use. By extension, the expression also refers to the storage of matter containing energy, therefore, the storage material. This sector continues to be the subject of research, whether for sensible, latent, or thermochemical storage applications, always looking for promising materials having both ecological and economic criteria and good thermal conductivity [15][16][17][18][19][20]. The storage of thermal energy mainly concerns the heat coming from the sun. More recently, the storage of the waste heat produced by certain industries (metallurgical industry, gas plant, incineration plant and others) has also been investigated. Thermal energy storage technologies can be classified into various categories according to different criteria (see [Figure 2](#)). If the criterion is the temperature range, storage systems are divided into "heat storage" and "cold storage" [21][22]. In the case where the criterion is the duration of storage, two classes are considered: "long-term storage" and "short-term" storage. On the other hand, if the criterion is the condition of the storage material, there are three main types: "sensible heat storage", "latent heat storage", and "thermochemical heat storage" [23].

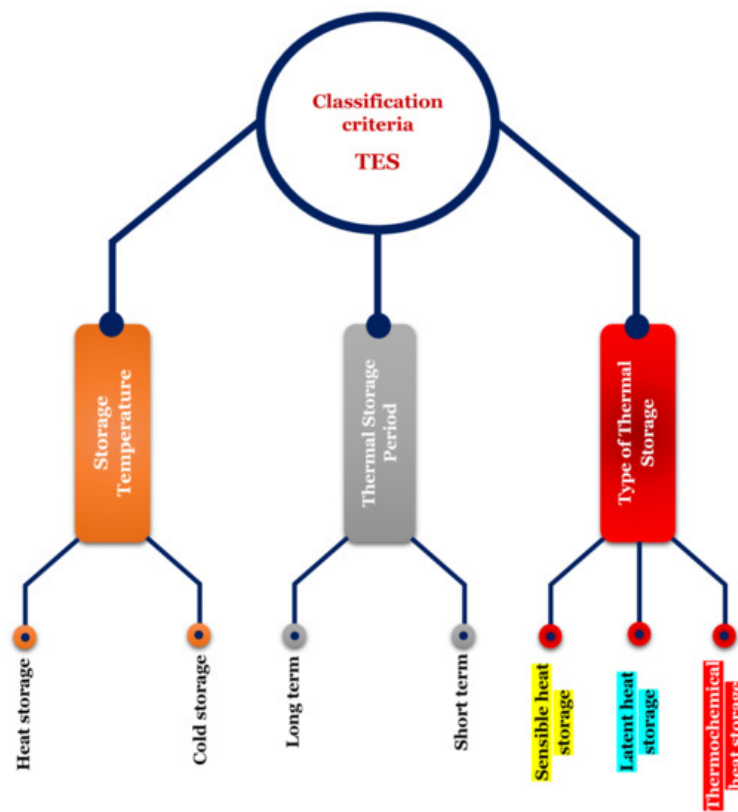


Figure 2. Classification of thermal energy storage systems.

Table 1 lists the characteristics of the three types of thermal energy storage presented. Six fundamental parameters were chosen: energy density, storage temperature, storage time, energy transport, system maturity, and system implementation complexity. Currently, SHS is the most mature thermal energy storage process. Without changing the phase of a material, the SHS system stores energy, and the energy storage density depends on the material's specific heat, mass of the heat storage medium, and the increase in temperature. Low cost and thermal stability are desirable characteristics of heat storage in the SHS system, while the SHS system's drawbacks are the need for a larger volume, higher thermal loss, unbalanced discharge temperature, and smaller energy storage density than the LHS and TCES systems. During the phase change of a material, the LHS system stores heat. Solid–solid, solid–liquid, or solid–gas can be the phase transition ^{[24][25]}. The quantity of heat retained depends on the latent heat of the material in the LHS method.

Table 1. List of thermal energy storage systems and their characteristics.

SHS System	LHS System	TCES System	
Principle description	<p>SHS storage involves increasing the temperature of an element and recovering this energy by dropping its temperature during the discharge phase. Then, we use the heat capacity, C_p, of the element, which is the amount of energy needed, per unit mass, to increase (or decrease) its temperature by 1 °C. The discharge temperature cannot be higher than the charge temperature. For applications where the operating temperature is between 0 and 100 °C, the most widely-used material is water, for example, in the domestic hot water tank of a home. Indeed, it is a non-toxic and inexpensive product. There is also the use of certain rocks or concrete. Beyond 100 °C, it is possible to use solid elements such as concrete at high temperatures or refractory ceramics, but the necessary volumes are important. Generally, we can find liquid storage systems for molten salts, pressurized water, or organic oils. For high temperature applications, molten salts are the most widely used material. This is due to their high volumetric heat capacity, a high boiling point, high temperature stability, and their vapor pressure being close to zero. Additionally, they are relatively cheap, readily available, neither toxic nor flammable, and can act as a heat transfer fluid as well as a TES material. However, they have certain disadvantages: they have a relatively high melting point (generally >200 °C), which results in them solidifying in pipes in the absence of a heat source and thus necessitates the installation of antifreeze systems; they also have high viscosity and low thermal conductivity compared to other fluids [26].</p>	<p>LHS is the amount of energy required to change the state of a solid, liquid or gas, called phase change material, PCM. In LHS systems, common transformations are from solid to liquid or from liquid to gas. The temperature range corresponding to the phase change of a PCM should be relatively small (20 to 80 °C). The materials used in LHS are numerous and allow working over a wide temperature range (example: 0 °C for water; 318 °C for sodium hydroxide). Latent heat storage in 'low' temperature range below 220 °C, 'medium' range up to 420 °C, and 'high' range greater than 420 °C is associated with a solar power tower as the point focus system. Materials for potential use as PCMs are mostly organic compounds, inorganic salts, and their eutectics. Inorganic materials such as salt hydrates, metals, and eutectics as well as organic compounds such as paraffin waxes, esters, acids, and alcohols have been studied [27]. According to the literature, molten salts have received more attention for heat storage applications than molten metals and alloys [28].</p>	<p>TCES involves reversible reactions, endothermic in one direction and exothermic in the other direction. These may be physical or chemical phenomena, described as follows: $A + \Delta H \rightleftharpoons B + C$ During the storage process, the charging phase corresponds to an endothermic decomposition reaction of a chemical element A into two products B and C stored separately at room temperature. The phase of discharge corresponds to the exothermic synthesis of the chemical element A by association of the two components B and C. It can correspond to physisorption or chemisorption phenomena, but in all cases, the heat released comes from the breaking of the bonds between the various components. TCES can be applied to energy storage at less than 100 °C and between 100–400 °C, the physisorption being characterized by a low enthalpy (<50 kJ/mol of material) and chemisorption, by a high enthalpy (>100 kJ/mol of material). TCES is defined according to two criteria: is the process open or closed, and is the reactor integrated or separate from the storage system. In a closed circuit, the storage of the sorbate is an internal element of the process. In an open circuit, in contrast, there is a transfer of material with the outside of the process in order to supply the sorbate to the reactor. In both cases, sorbent storage is a component of the system.</p>
Volumetric energy density storage	Small (15–50 kWh/m ³)	Medium (50–100 kWh/m ³)	High (100–700 kWh/m ³)
Gravimetric energy density storage	Small (0.02–0.03 kWh/kg)	Medium (0.05–0.1 kWh/kg)	High (0.5–1.0 kWh/kg)
Capacity	10–50 (kWh/t)	50–100 (kWh/t)	120–250 (kWh/t)
Power	0.001–10.0 (MW)	0.001–1.0 (MW)	0.01–1.0 (MW)
Efficiency	50–90%	75–90%	75–100%
Cost	0.1–10 (€/kWh)	10–50 (€/kWh)	8–100 (€/kWh)
Storage temperature	Charging step temperature	Charging step temperature	Ambient temperature
Storage period	Limited due to thermal losses to surroundings	Limited due to thermal losses to surroundings	Theoretically unlimited
Energy transport	Shorter distance	Shorter distance	Theoretically long distance
Maturity	Industrial scale	Pilot-scale	Laboratory and pilot-scale
Technology	Simple	Simple	Complex

The LHS system has a higher heat storage density compared to the SHS, is dense, and has a steady discharge temperature. Low thermal conductivity, flammability of certain organic materials, and corrosiveness are the main drawbacks of the LHS system [13][29]. Via the sorption process and chemical reaction, a thermochemical energy storage (TCES) system stores energy. Endothermic and exothermic reactions are the chemical reactions for charging and discharging heat, respectively.

In the literature, two types of TCES systems are addressed: sorption-based TCES and reaction-based TCES. High energy storage density and the ability to store energy with minor losses for longer periods are the two key advantages of a TCES approach. For these reasons, TCES has attracted the interest of researchers around the world.

3. Outlook

Research on sorption heat storage still needs more in-depth investigation at the micro- and macro-scale levels. Much research is continuing in this subject to propose and find a suitable adsorbent material for commercial application. The current review paper summarized the use of salts, composites, and binary salt as sorbents for sorption heat storage by questioning its production status from various points of view. Research work is still in progress in the effort to address the strategic issues associated with this technology. At present, researchers are proposing a new promising approach to solve the disadvantage of pure salt hydrates in the TES system by using some composite materials based salts. However, heat and mass transport problems can also occur due to:

- Decrease of unoccupied pores;
- Probable deliquescence;
- Leakage of salt from the composite; and
- Degradation.

Major conclusions of study and issues that should be addressed in future with recommendations are mentioned as follows in order to reach commercial application:

- In terms of material, the strategic task is to decrease the prices of the available materials, with the aim to make TES sorption systems more competitive. At this stage, many efforts are devoted to the use of cheaper raw materials and diminishing the hydrophilicity of traditional zeolites, which needs high energy consumption (desorption temperature) that is unattainable, for instance, by traditional solar thermal collectors.
- A deep examination on sorption heat storage is strongly required at diverse scales and several conditions can help to compare experimental studies in a standardized way. Recently, metal organic frameworks (MOFs) and aluminophosphates have shown a remarkable result that needs more focus, thanks to their promising features. Materials for TES sorption systems require more research to discover an appropriate active material with acceptable energy density, hydrothermal stability, and cyclability under the operating conditions of the device.
- Composite materials are being studied in order to diminish the instabilities at salt hydrate material levels. If a high enough desorption temperature is achieved, the host matrices can be made of a porous material that can also act as an adsorbent. Small pore sizes, which are needed for the matrix to participate in the sorption process, result in little salt impregnated in the matrix. Ineffective materials including expanded graphite, sand, silica gel, and vermiculite, on the other hand, have been studied solely for structural support. Numerous studies have been published, but further work is being done to find promising working pairs. Diminished mass transport inside the matrix pores as well as salt deliquescence or overhydration can lead to active material leakage. Finally, the experimental conditions of the examined studies are heterogeneous and some of them are far from the characteristic conditions of low-temperature heat storage. Furthermore, more research is required to fully and deeply comprehend the kinetics and mechanisms that have occurred by using composite materials in TES sorption systems.
- For upcoming studies on sorption heat storage systems, some critical points also should be considered: For instance, the energy density at different stages of the search need to be determined by setting a common reference temperature. In addition, along with the energy density, the required volume used must be defined.
- Only a few studies have concentrated on the economic viability of the systems. This is partly due to the fact that analysis is always at the material and laboratory scale; thus, broad economic surveys will possibly lead to misleading

results.

- The economic feasibility of the system has not been well examined because there are many challenges not yet achieved at material and lab-scales. Consequently, broad economic surveys would likely lead to ambiguous outcomes. Nevertheless, the central indicators allied to material cost, system complexity, and auxiliary energy consumption system should be considered in order to have an idea about the estimation of system cost-effectiveness.
- The cost of materials will already give an idea of how profitable and potential the system will be in a given application. For cost estimation, all components and auxiliary systems must be considered when increasing the scale. Supplementary economic considerations that can be highlighted at commercial scale (Prototype) linked to system operations such as lifetime and maintenance costs may perhaps also be involved to evaluate the rentability analysis.

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