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A Critical Review of Thermochemical Energy Storage Systems

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Abstract: Thermal energy storage (TES) is an advanced technology for storing thermal energy that can mitigate environmental impacts and facilitate more efficient and clean energy systems. Thermochemical TES is an emerging method with the potential for high energy density storage. Where space is limited, therefore, thermochemical TES has the highest potential to achieve the required compact thermal energy storage. Thermochemical TES is presently undergoing research and experimentation. In order to develop an understanding of thermochemical TES systems and to improve their implementation, comprehensive analyses and investigations are required. Here, principles of thermochemical TES are presented and thermochemical TES is critically assessed and compared with other TES types. Recent advances are discussed.

Keywords: Thermal energy storage, thermochemical energy storage, compact TES.

1. INTRODUCTION

Societal energy demands are presently increasing while fossil fuel resources, which dominate most national energy systems, are limited and predicted to become scarcer and more expensive in coming years [1, 2]. Furthermore, many concerns exist regarding the environmental impacts associated with increasing energy consumption, such as climate change and atmospheric pollution. Greenhouse gas (GHG) emissions are considered the main cause of climate change, and agreements to limit them, such as the Kyoto Protocol, have been developed [3].

Changes are required in energy systems, partly through the adoption of advanced energy technologies and systems where advantageous, to address serious environmental concerns. The anticipated worldwide increase in energy demand and concern regarding environmental problems is fostering the utilization of more efficient and cleaner energy technologies, in relevant applications. Examples include advanced systems for waste energy recovery and energy integration.

An important technology that can contribute to avoiding environmental problems and increasing the efficiency of energy consumption and that has widespread applications is thermal energy storage (TES).

Thermal energy storage is defined as the temporary holding of thermal energy in the form of hot or cold substances for later utilization. TES is a significant technology in systems involving renewable energies as well as other energy resources as it can make their operation more efficient, particularly by bridging the period between periods when energy is harvested and periods when it is needed. That is, TES is helpful for balancing between the supply and demand of energy [4]. Thus, TES plays an important role in increasing the contribution of various types of renewable energy in the energy mix of regions and countries.

Various TES technologies and applications exist. The selection of a TES system for a particular application depends on many factors, including storage duration, economics, supply and utilization temperature requirements, storage capacity, heat losses and available space.

The main types of TES are sensible and latent. Sensible TES systems store energy by changing the temperature of the storage medium, which can be water, brine, rock, soil, etc. Latent TES systems store energy through phase change, e.g., cold storage water/ice and heat storage by melting paraffin waxes. Latent TES units are generally smaller than sensible storage units. More compact TES can be achieved based on storages that utilize chemical reactions. Such thermochemical storage systems, which constitute the focus of this article, have recently been the subject of increased attention and could be especially beneficial where space is limited.

Thermochemical TES systems are not yet commercial and research and development is required to better understand and design these technologies and to resolve other practical aspects before commercial implementation can occur [5]. In particular, a better understanding of their efficiencies is required. In this article, principles of thermochemical TES and recent advances are presented, and thermochemical TES is critically assessed and compared with other TES types. Also, advantages and disadvantages of thermochemical TES are considered as they relate to other TES types. The objective is to improve understanding and thereby support development and ultimate implementation of the thermochemical TES technology.

2. THERMAL ENERGY STORAGE

The importance of thermal energy storage has motivated many researchers to study various aspects of the technology

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and the formation of a related task at the International Energy Agency [5]. Of the different types of thermal energy storage, sensible heat storages usually are applied for large plants, e.g. aquifer TES [6], while latent heat storage is typically appropriate for low-temperature heat sources and narrow temperature intervals [7].

There are three main types of TES systems [5]:

- Sensible
- Latent
- Chemical (sorption and thermochemical)

2.1. Sensible TES

In sensible TES systems, energy (or heat) is stored/released by heating/cooling a liquid or solid storage material through a heat transfer interaction. The amount of energy input to a TES in a sensible heat system is related to the mass of storage material and its heat capacity as well as the temperature difference of the storage medium between its initial and final states. This heat transfer Q can be expressed as:

$$Q = mC_p\Delta T$$

where m and C_p are denote the mass and specific heat of the storage material and ΔT is the temperature difference before and after the storage operation. Examples of materials typically used as a storage medium are water, air, oil, rocks, brine, concrete, sand and soil.

2.2. Latent TES

Latent heat involves the change of a substance from one phase to another at a fixed temperature. In latent TES systems, energy is stored during the phase change (e.g. melting, evaporating and crystallization). Due to the specific heat of a typical medium and the high enthalpy change during phase change, the latent heat change is usually greater than the sensible heat change for a given system size. Latent heat storage materials are usually useful over a small temperature range [5].

The stored energy during a latent storage process can be evaluated as:

$$Q = mL$$

where m denotes the mass and L is the specific latent heat of the phase change material (PCM). Examples of PCMs are water/ice, paraffin and eutectic salts. An example of an industrial PCM is the hand warmer (sodium acetate trihydrate). PCMs are usually packed in tubes, plastic capsules, wall board and ceilings and they are supplied mainly in three shapes: powder, granulate and board.

2.3. Chemical Energy Storage

The chemical TES category includes sorption and thermochemical reactions. In thermochemical energy storage, energy is stored after a dissociation reaction and then recovered in a chemically reverse reaction. Thermochemical energy storage has a higher storage density than the other types of TES, allowing large quantities of energy to be stored using small amounts of storage substances. Energy storage based on chemical reactions is particularly appropriate for long-term storage applications, e.g., seasonal storage of solar heat, because the process involves almost no energy losses during the storing period. Storage is usually done at ambient temperatures.

Sorption systems (adsorption and absorption) are based on a chemical processes and thus are also considered chemical heat storage. Adsorption occurs when an adsorptive accumulates on the surface of an adsorbent and shapes a molecular or atomic layer. The adsorptive can be a liquid or gas while the adsorbent can be a solid or liquid. Absorption is a process that occurs when a substance is distributed into a liquid or solid and forms a solution.

3. THERMOCHEMICAL TES

The principles of thermochemical energy storage systems, as well as the relevant components and processes, are described.

3.1. Principles of Thermochemical Energy Storage

The main principle of thermochemical TES is based on a reaction that can be reversed:

$$C + \text{heat} \rightleftarrows A + B$$

In this reaction, a thermochemical material (C) absorbs energy and is converted chemically into two components (A and B), which can be stored separately. The reverse reaction occurs when materials A and B are combined together and C is formed. Energy is released during this reaction and constitutes the recovered thermal energy from the TES. The storage capacity of this system is the heat of reaction when material C is formed.

3.2. Thermochemical Energy Storage Components and Processes

During the thermochemical storage reaction, expressible as $C + \text{heat} \rightleftarrows A + B$, C is the thermochemical material (TCM) for the reaction, while materials A and B are reactants. Substance A can be a hydroxide, hydrate, carbonate, ammoniate, etc. and B can be water, CO, ammonia, hydrogen, etc. There is no restriction on phases, but usually C is a solid or a liquid and A and B can be any phase. In general, a TES cycle includes three main processes:

- Charging
- Storing
- Discharging

These three processes are illustrated for thermochemical energy storage in Fig. (**1**), and are described individually below:

Charging: The charging process is endothermic. Thermal energy is absorbed from an energy resource, which could be a renewable energy resource and/or conventional energy sources like fossil fuels. This energy is used for dissociation of the thermochemical material, and is equivalent to the heat of reaction or enthalpy of formation. After this process, two materials (A and B) with different properties

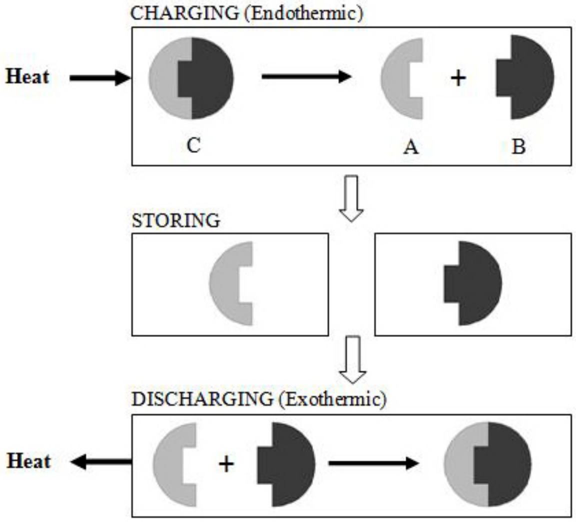

Fig. (1). Processes involved in a thermochemical energy storage cycle: charging, storing and discharging.

are formed that can be stored. The reaction during charging can be written as:

$$C + heat \rightleftarrows A + B$$

Storing: After the charging process, components A and B are separately stored with little or no energy losses. The materials are usually stored at ambient temperatures, leading to no thermal losses (except during the initial cooling of components A and B after charging). Any other energy losses are due to degradation of the materials.

Discharging: During this process, A and B are combined in an exothermic reaction. The energy released from this reaction permits the stored energy to be recovered. After discharging, component C is regenerated and can be used again in the cycle. The discharging reaction can be written as:

$$A + B \rightarrow C + heat$$

3.3. Recent Developments in Thermochemical TES

A comprehensive review of thermochemical energy storage [8] describes the main concepts, criteria for choosing appropriate storage media and candidate reaction pairs. Due to the high energy density and compact nature of thermochemical energy storage, this type of TES is considered by many to be promising for residential and commercial buildings. Heat storage based on chemical reactions can be applied to heating and cooling in small and large buildings as well. Further, thermochemical TES is useful for short durations as well as longer periods, as used in seasonal thermal storage.

Several investigations of thermochemical TES have been reported. Weber and Dorer analyzed long-term heat storage using a closed sorption system with NaOH and water as the working pair and compared the results with a conventional storage system, focusing on system volume [9]. An investigation based on bromide strontium as the reactant and water as the working fluid [10], in a system using flat plate solar collectors and applied to direct floor heating, demonstrated the relations between the attained power levels and the heating storage capacities of reactive composites. Mauran *et al.* [11] analyzed experimentally the same working pair for heating and cooling purposes (heating in winter or mid-season and cooling in summer). Zondag *et al.* [12] characterized magnesium sulphate as a storage media and examined the cycling behavior of $MgSO_4$ and the dehydration temperature of the reactant. Thermal energy storage based on the $Ca(OH)_2$ and CaO cycle is another example of thermochemical energy storage, and the reversibility and efficiency of this system was investigated in Azpiazu *et al.* [13]. Thermochemical energy storage based on the chemical pair ammonia and water has been investigated in conjunction with a solar thermal plant. General characteristics of this working pair as well as the dissociation and synthesis reactor were studied in [14] and the optimization of a related heat recovery device has been reported [15].

4. CRITICAL ASSESSMENT AND COMPARISON OF THERMOCHEMICAL TES SYSTEMS

Thermochemical TES is assessed and compared to other types of TES, considering thermochemical material candidates, factors affecting their selection and primary advantages.

4.1. Advantages of Thermochemical Energy Storage

Thermochemical TES systems have several advantages over other types of TES:

- Components (A and B) can usually be stored separately at ambient temperature, after cooling to ambient conditions subsequent to their formation. Therefore,

Table 1. Promising Materials for Thermochemical Energy Storage [8, 16]

Thermochemical Material (C)	Solid Reactant (A)	Working Fluid (B)	Energy Storage Density of Thermochemical Material (GJ/m^3)	Charging Reaction Temperature (°C)
$MgSO_4{\cdot}7H_2O$	$MgSO_4$	$7H_2O$	2.8	122
$FeCO_3$	FeO	CO_2	2.6	180
$Ca(OH)_2$	CaO	H_2O	1.9	479
$Fe(OH)_2$	FeO	H_2O	2.2	150
$CaCO_3$	CaO	CO_2	3.3	837
$CaSO_4{\cdot}2H_2O$	$CaSO_4$	$2H_2O$	1.4	89

there is little or no heat loss during the storing period and, as a consequence, insulation is not needed.

- As a result of the low heat losses, thermochemical TES systems are especially suitable for long-term energy storage (e.g., seasonal storage).
- Thermochemical materials have higher energy densities relative to PCMs and sensible storage media. Because of higher energy density, thermochemical TES systems can provide more compact energy storage relative to latent and sensible TES. This attribute is particularly beneficial where space for the TES is limited or valuable.

4.2. Thermochemical Storage Material Candidates

Some promising thermochemical storage material candidates that have been recently identified are listed in Table **1**, along with values of energy density and reaction temperature. Energy density and reaction temperature are two important factors, among others, for a thermochemical material for application in thermochemical TES systems.

4.3. Factors Affecting the Choice of Thermochemical Material

Several parameters should be examined in selecting a thermochemical material, as they affect its use in TES systems. The relevant factors include:

- Cost
- Cycling behavior (reversibility and degradation over large numbers of cycles)
- Availability
- Toxicity and safety
- Corrosiveness
- Energy storage density
- Reaction temperature
- Reaction rate
- Ability to be engineered into a practical system (e.g., heat transfer characteristics and flow properties)

5. COMPARISON OF THERMOCHEMICAL TES AND OTHER TES TYPES

The different types of thermal energy storage systems are quantitatively contrasted and compared in Table **2**, considering a range of relevant performance parameters and factors. It is evident that each has different operating characteristics, advantages and disadvantages. For different applications, different TESs can be the most appropriate choice.

Table 2. Comparison of Different Types of TES Based on Various Performance Factors*

Performance Parameter	Type of Thermal Energy Storage		
	Sensible TES	**Latent TES**	**Chemical TES (Sorption and Thermo-chemical)**
Temperature range	Up to: 110 °C (water tanks) 50 °C (aquifers and ground storage) 400 °C (concrete)	20-40 °C (paraffins) 30-80 °C (salt hydrates)	20-200 °C
Storage density	Low (with high temperature interval): 0.2 GJ/m^3 (for typical water tanks)	Moderate (with low temperature interval): 0.3-0.5 GJ/m^3	Normally high: 0.5-3 GJ/m^3
Lifetime	Long	Often limited due to storage material cycling	Depends on reactant degradation and side reactions
Technology status	Available commercially	Available commercially for some temperatures and materials	Generally not available, but undergoing research and pilot project tests
Advantages	Low cost Reliable Simple application with available materials	Medium storage density Small volumes Short distance transport possibility	High storage density Low heat losses (storage at ambient temperatures) Long storage period Long distance transport possibility Highly compact energy storage
Disadvantages	Significant heat loss over time (depending on level of insulation) Large volume needed	Low heat conductivity Corrosivity of materials Significant heat losses (depending on level of insulation)	High capital costs Technically complex

* Adapted from several sources including http://www.preheat.org/technology/ and [8].

CONCLUSIONS

A comprehensive review of various types of TES systems, highlighting thermochemical TES, has been presented. Principles of thermochemical TES and recent advances have been reported. The possibility of achieving more compact systems, little energy losses during the storing operation and higher energy densities compared to other types of TES are the most prominent advantages of thermochemical TES systems. Further research is needed to improve understanding of the scientific and engineering characteristics of thermochemical TES systems and to help improve various aspects relating to the performance and implementation of these systems. The thermochemical material is a critical component of such systems. The cyclic behavior and degradation of thermochemical materials, as well as their cost, availability, durability and energy density, are important parameters affecting the selection of a thermochemical material. Further research is needed on these topics, as well as on design factors, safety, size and efficiency, installation, maintenance and economics for thermochemical TES systems. Also, comprehensive analyses of these systems based on energy and exergy are needed, as such assessments can assist in design optimization and improvement, and such work is the subject of ongoing research by the authors.

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REFERENCES

[1] Rasthal, J.E.; Drennen, T.E. *Pathways to a Hydrogen Future,* 3rd ed.; Elsevier: UK, **2007**.

[2] Rahm, D. *Sustainable Energy and the States, Essay on Politics Markets and Leadership*, 1st ed.; McFarland: North Carolina, **2002**.

[3] Fuglestvedt, J.S.; Hailemariam, K.; Stuber, N. Alternatives to the global warming potential for comparing climate impacts of emissions of greenhouse gases. *Clim. Change,* **2005**, *68*(3), 281-302.

[4] Dincer, I.; Rosen, M.A. *Thermal Energy Storage: Systems and Applications*, 2nd ed.; Wiley: UK, **2011**.

[5] International Energy Agency (IEA). *Compact Thermal Energy Storage: Material Development and System Integration*. Annex text (draft), Task 42, Annex 28, Solar Heating and Cooling Programme, **2008**.

[6] Dincer, I.; Dost, S.; Li, X. Performance analyses of sensible heat storage systems for thermal applications. *Int. J. Energy Res.,* **1997**, *21* (12), 1157-1171.

[7] Shilei, L., Guohui, F.; Neng, Z.; Li, D. Experimental study and evaluation of latent heat storage in phase change materials wallboards. *Energy Build.,* **2007**, *39*(10), 1088-1091.

[8] Wettermark, G. *Thermochemical Energy Storage*, Proceeding of NATO Advanced Study Institute on Energy Storage Systems, Cesme, Turkey, June 27- July 8, **1988**; pp. 673-681.

[9] Weber, R.; Dorer, V. Long-term heat storage with NaOH. *Vacuum,* **2008**, *82*(7), 708-716.

[10] Lahmidi, H.; Mauran, S.; Goetz, V. Definition, test and simulation of a thermochemical storage process adapted to solar thermal systems. *Sol. Energy,* **2006**, *80* (7), 883-893.

[11] Mauran, S.; Lahmidi, H.; Goetz, V. Solar heating and cooling by a thermochemical process: first experiments of a prototype storing 60 kWh by a solid/gas reaction. *Solar. Energy,* **2008**, *82*(7), 623-636.

[12] Zondag, H.; van Essen, M.; He, Z.; Schuitema, R.; van Heldan, W. *Characterization of $MgSO_4$ for Thermochemical Storage*. Second International Renewable Energy Storage Conference (IRES II), Bonn, Germany. November 19-21, **2007**.

[13] Azpiazu, M.N.; Morquillas, J.M.; Vazquez, A. Heat recovery from a thermal energy storage based on the $Ca(OH)_2/CaO$ cycle. *Appl. Therm. Eng.,* **2003**, *23*(6), 733-741.

[14] Lovergrove, K.; Luzzi, A.; Kreetz, H. A solar-driven ammonia-based thermochemical energy storage system. *Solar Energy,* **1999**, *67*(4), 309-316.

[15] Kreetz, H.; Lovergrove, K. Theoretical analysis and experimental results of a 1 kW_{chem} ammonia synthesis reactor for a solar thermochemical energy storage system. *Solar Energy,* **1999**, *67*(4), 287-296.

[16] Visscher, K.; Veldhuid, J.B.J. *Comparison of Candidate Material for Seasonal Storage of Solar Heat through Dynamic Simulation of Building and Renewable Energy System*, Proceedings of Ninth International IBPSA Conference, Montreal, Canada, August 15-18, **2005**; pp. 1285-1292.

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