

# Thermochemical Energy Storage Systems: Modelling, Analysis and Design

By

Ali Haji Abedin

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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 TES. Principles of thermochemical TES are presented and thermochemical TES is critically assessed and compared with other TES types. The integration of TES systems with heating, ventilating and air conditioning (HVAC) applications is examined and reviewed accounting for various factors, and recent advances are discussed. Thermodynamics assessments are presented for general closed and open thermochemical TES systems. Exergy and energy analyses are applied to assess and compare the efficiencies of the overall thermochemical TES cycle and its charging, storing and discharging processes. Examples using experimental data are presented to illustrate the analyses. Some important factors related to design concepts of thermochemical TES systems are considered and preliminary design conditions for them are investigated. Parametric studies are carried out for the thermochemical storage systems to investigate the effects of selected parameters on the efficiency and behavior of thermochemical storage systems.

## **Keywords**

Thermal Energy Storage; Thermochemical Energy Storage; Energy Efficiency; Exergy Efficiency, First Law Efficiency; Second Law Efficiency; Exergy

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## **Dedication**

This thesis is dedicated to my beloved wife, Samira.

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## Nomenclature

$C_p$	specific heat at constant pressure (kJ/kg K)
$E$	energy (kJ)
$h$	specific enthalpy (kJ/kg)
$m$	mass of working fluid (kg)
$M$	mass of reactant (kg)
$n$	number of moles (-)
$P$	pressure (kPa)
$Q$	heat (kJ)
$s$	specific entropy (kJ/kg K)
$T$	temperature (°C or K)
$V$	volume (m <sup>3</sup> )

## Subscripts

$0$	reference environment
$ad$	adsorption
$c$	charging
$ch$	chemical
$d$	discharging
$ds$	desorption

<i>D</i>	destruction
<i>e</i>	element
<i>o</i>	overall
<i>ph</i>	physical
<i>s</i>	solid, storing
<i>tot</i>	total

### **Greek Letters**

$\Delta G_f$	Gibbs energy of formation (kJ/mol)
$\Delta H$	enthalpy change of reaction (kJ)
$\Delta E$	energy accumulation (kJ)
$\Delta \epsilon$	exergy accumulation (kJ)
$\epsilon$	exergy (kJ)
$\epsilon_{chn}$	standard chemical exergy of a compound (kJ/mol)
$\epsilon_{chne}$	standard chemical exergy of an element (kJ/mol)
$\eta$	energy efficiency (-)
$\rho$	density (kg/m <sup>3</sup> )
$\psi$	exergy efficiency (-)

## **Acronyms**

TES	Thermal Energy Storage
GHG	Greenhouse Gas
PCM	Phase Change Material
TCM	Thermochemical Material
HVAC	Heating Ventilating and Air Conditioning
DHW	Domestic Hot Water
CTES	Cooling Thermal Energy Storage
EES	Engineering Equation Solver
COP	Coefficient Of Performance
ATES	Aquifer Thermal Energy Storage
DLSC	Drake Landing Solar Community
BTES	Borehole Thermal Energy Storage
GWP	Global Warming Potential
ODP	Ozone Depletion Potential

# Chapter 1

## Introduction

### 1.1 Thermal Energy Storage

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 (Rasthal and Drennen, 2007; Rahm, 2002). 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 (Fuglestvedt et al., 2005).

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 (Dincer and Rosen, 2002). Thus, TES plays an important role in increasing the contribution of various types of renewable energy in the energy mix of regions and countries.

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 chapter, have recently been the subject of increased attention and could be especially beneficial where space is limited.

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.

Thermochemical TES systems are not yet commercial and more scientific research and development is required to better understand and design these technologies and to resolve other practical aspects before commercial implementation can occur (IEA, 2008). In particular, a better understanding of their efficiencies is required.

The integration of TES systems with heating, ventilating and air conditioning (HVAC) applications is an interesting topic to be investigated. In HVAC systems,

TES can shift electrical demand from peak (usually daytimes) to off-peak (often nighttime) periods, often reducing electrical bills. Recently, TES utilization has increased for heating and cooling purposes in various thermal applications. Various types of integrations of TES systems with HVAC applications can be reviewed and recent advances can be discussed.

To assess the effectiveness with which energy resources are used in conjunction with thermal energy storage, the first and second laws of thermodynamics need to be utilized. Exergy analysis, which is based on these laws, can assist in comparing, improving and optimizing TES designs better than the more conventional energy analysis and yields more meaningful efficiencies (Rosen and Dincer, 2003). Second law methods in general and exergy analysis in particular, are best used in place of or in conjunction with the first law methods (i.e., energy analysis) to gain understanding about energy systems.

The design of thermochemical energy storage systems is complex and requires appropriate consideration of many factors. Generally, many criteria need to be evaluated by engineers in engineering design such as cost, environmental impact, safety, reliability, efficiency, size, and maintenance. These factors need to be considered in designing thermochemical TES systems.

Parametric studies can be carried out for the thermochemical storage systems to investigate the effects of selected parameters on the efficiency and behavior of thermochemical storage systems.

## **1.2 Objectives and Scope**

In this study, a comprehensive review of various types of TES systems, highlighting thermochemical TES, are presented. Principles of thermochemical TES and recent

advances are considered, 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 of this comparison is to improve understanding and thereby support development and ultimate implementation of the thermochemical TES technology.

Case studies of integrating TES with HVAC applications in heating and cooling systems are described which illustrate practical applications as well as laboratory-scale examples for new advances, with an objective of supporting ongoing research into increasing TES compactness via thermochemical methods.

In order to help understand and contrast efficiencies for the various processes occurring in TES systems, exergy analysis is applied, in addition to energy analysis, to closed and open thermochemical TES systems to specify the locations and reasons of thermodynamic losses in TES systems. Energy and exergy analyses can assist efficiency improvement efforts.

The key objective in designing a thermochemical storage system is to charge and discharge the storage in a controlled and optimal way, including having an appropriate overall efficiency. Designing such systems necessitates the application of engineering thermodynamics, heat and mass transfer, fluid mechanics, economics, reaction kinetics, and other subjects. In order to understand the relation among various parameters affecting the performance of a thermochemical energy storage system, parametric analyses are performed.

# Chapter 2

## Background

### 2.1 Thermal Energy Storage Classification

The importance of thermal energy storage has motivated many researchers to study various aspects of the technology and the formation of a related task at the International Energy Agency (IEA, 2008). Of the different types of thermal energy storage, sensible heat storages usually are applied for large plants, e.g. aquifer TES (Dincer et al., 1997), while latent heat storage is typically appropriate for low-temperature heat sources and narrow temperature intervals (Shilei et al., 2007). There are three main types of TES systems (IEA, 2008):

- Sensible
- Latent
- Chemical (sorption and thermochemical)

#### 2.1.1 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 (Dincer and Rosen, 2002). This heat transfer can be expressed as

$$Q = mC_p \Delta T \tag{2.1}$$

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

### **2.1.2 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 media 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 (IEA, 2008). The stored energy during a latent storage process can be evaluated as

$$Q = mL \tag{2.2}$$

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, eutectic salts, and some polymers. 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.

### **2.1.3 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.

### **2.1.3.1 Thermochemical TES**

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

#### **2.1.3.1.1 Principles of Thermochemical Energy Storage**

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



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 A and B are combined together and C is formed.

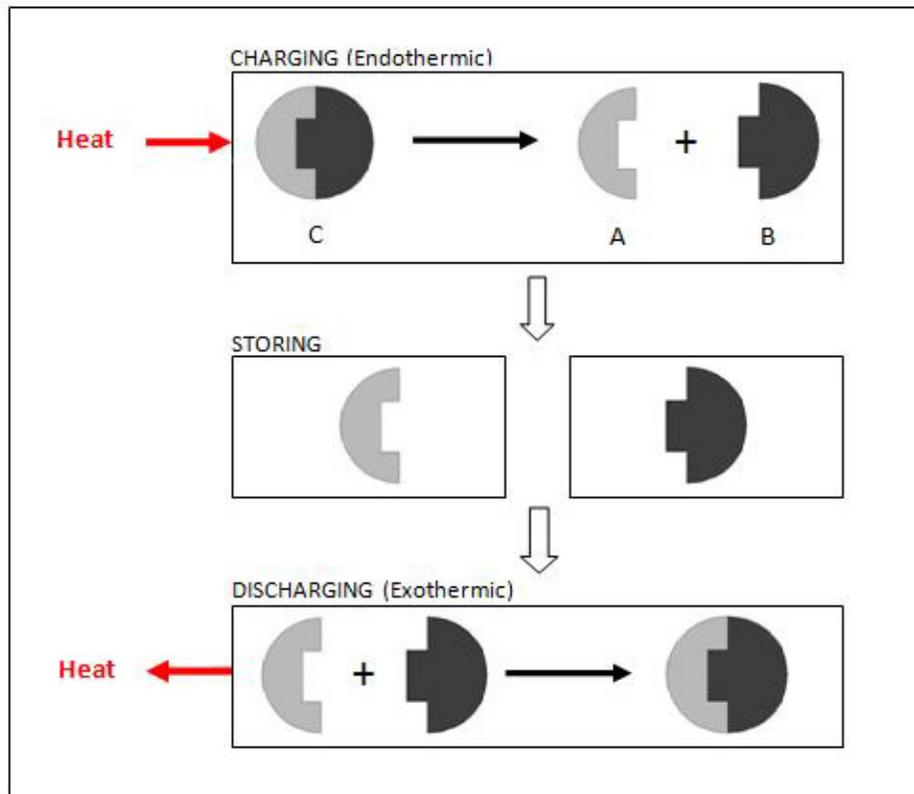
Energy is released during this reaction and constitutes the recovered thermal energy from the TES. The storage capacity of this system is the heat of reaction when C is formed.

### **2.1.3.1.2 Thermochemical Energy Storage Components and Processes**

During the thermochemical storage reaction, expressible as  $C + \text{heat} \rightleftharpoons A + B$ , C is the thermochemical material (TCM) for the reaction, while 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 Figure 2.1, and are described individually below:



**Figure 2.1. Processes involved in a thermochemical energy storage cycle: charging, storing and discharging.**

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



**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



### 2.1.3.1.3 Recent Developments in Thermochemical TES

A comprehensive review of thermochemical energy storage describes the main concepts, criteria for choosing appropriate storage media and candidate reaction pairs (Wettermark, 1989). 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 et al. (2008) 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. An investigation based on bromide strontium as the reactant and water as the working fluid, 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 (Lahmidi et al.,

2006). Mauran et al. (2008) analyzed experimentally the same working pair for heating and cooling purposes (heating in winter or mid-season and cooling in summer). Zondag et al. (2007) characterized magnesium sulphate as a storage media and examined the cycling behavior of  $\text{MgSO}_4$  and the dehydration temperature of the reactant. Thermal energy storage based on the  $\text{Ca}(\text{OH})_2$  and  $\text{CaO}$  cycle is another example of thermochemical energy storage, and the reversibility and efficiency of this system was investigated (Azpiazu et al., 2003). 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 (Lovergrove et al., 1999) and the optimization of a related heat recovery device has been reported (Kreetz and Lovergrove, 1999).

An assessment based on exergy analysis determines the values of various energy and material streams in terms of their work potential or quality (Kreetz and Lovergrove, 2002). Exergy analysis has been applied widely in recent decades, and exergy analyses of various types of TES systems have been reported. For instance, one type of sensible TES (aquifer TES) has been investigated with exergy methods by Rosen (1999). Also, energy and exergy analyses for a latent TES using a PCM for a flat-plate solar collector have been performed for the charging period (Koca et al., 2008).

Although exergy assessments of thermochemical TES have not been reported to the best of the authors' knowledge, exergy analysis has been applied in some studies of thermochemical systems. For instance, an exergy analysis of an ammonia-based solar thermochemical power system was investigated (Lovergrove et al., 1999) and the exergy efficiency of the exothermic half of the cycle was analyzed; an exergy

efficiency of 71% was found to be achievable. Kreetz and Lovergrove (2002) performed an exergy analysis of the ammonia synthesis reactor. That study demonstrated the relation between reactor conditions and maximum exergy output rather than maximum thermal output. Nonetheless, the present authors feel that further work is needed to help attain viable designs for thermochemical TES systems.

### **2.1.3.2 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.

#### **2.1.3.2.1 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, 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.

### 2.1.3.2.2 Thermochemical Storage Material Candidates

Some promising thermochemical storage material candidates that have been recently identified are listed in Table 2.1, 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.

**Table 2.1. Promising materials for thermochemical energy storage.\***

Thermochemical material (C)	Solid reactant (A)	Working fluid (B)	Energy storage density of thermochemical material (C) (GJ/m <sup>3</sup> )	Charging reaction temperature (°C)
MgSO <sub>4</sub> ·7H <sub>2</sub> O	MgSO <sub>4</sub>	7H <sub>2</sub> O	2.8	122
FeCO <sub>3</sub>	FeO	CO <sub>2</sub>	2.6	180
Fe(OH) <sub>2</sub>	FeO	H <sub>2</sub> O	2.2	150
CaSO <sub>4</sub> ·2H <sub>2</sub> O	CaSO <sub>4</sub>	2H <sub>2</sub> O	1.4	89

\* Source: Visscher and Veldhuid (2005).

### 2.1.3.2.3 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)

### 2.1.3.3 Comparison of Thermochemical TES and Other TES Types

The different types of thermal energy storage systems are quantitatively contrasted and compared in Table 2.2, considering a range of relevant performance parameters and factors.

**Table 2.2. Comparison of different types of TES based on various performance factors.\***

Performance parameter	Type of thermal energy storage		
	Sensible TES	Latent TES	Chemical TES
Temperature range	Up to: <ul style="list-style-type: none"> <li>• 110°C (water tanks)</li> <li>• 50°C (aquifers and ground storage)</li> <li>• 400°C (concrete)</li> </ul>	20-40°C (paraffins) 30-80°C (salt hydrates)	20-200°C
Storage density	Low (with high temperature interval) 0.2 GJ/m <sup>3</sup> (for typical water tanks)	Moderate (with low temperature interval) 0.3-0.5 GJ/m <sup>3</sup>	Normally high 0.4-3 GJ/m <sup>3</sup>
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	<ul style="list-style-type: none"> <li>• Low cost</li> <li>• Reliable</li> <li>• Simple application with available materials</li> </ul>	<ul style="list-style-type: none"> <li>• Medium storage density</li> <li>• Small volumes</li> <li>• Short distance transport possibility</li> </ul>	<ul style="list-style-type: none"> <li>• High storage density</li> <li>• Low heat losses</li> <li>• Long storage period</li> <li>• Long distance transport possibility</li> <li>• Highly compact energy storage</li> </ul>
Disadvantages	<ul style="list-style-type: none"> <li>• Significant heat loss over time (depending on level of insulation)</li> <li>• Large volume needed</li> </ul>	<ul style="list-style-type: none"> <li>• Low heat conductivity</li> <li>• Corrosivity of materials</li> <li>• Significant heat losses (depending on level of insulation)</li> </ul>	<ul style="list-style-type: none"> <li>• High capital costs</li> <li>• Technically complex</li> </ul>

\* Adapted from several sources, including [www.preheat.org](http://www.preheat.org) and Wettermark (1989).

# Chapter 3

## Integrating Thermal Energy Storage and HVAC Systems

### 3.1 Introduction

Interest in TES is growing with the anticipated long-term worldwide increase in energy demand and environmental concerns are fostering the utilization of more efficient and cleaner energy technologies in relevant applications. Thermal energy storage fundamentally involves the temporary holding of thermal energy, often in the form of hot or cold substances, for later utilization. In HVAC systems, TES can shift electrical demand from peak to off-peak periods. In this chapter, various types of integrations of TES systems with HVAC applications are examined and reviewed and recent advances discussed. Case studies of heating and cooling systems are described which illustrate practical applications as well as laboratory-scale examples for new advances.

### 3.2 TES and HVAC Systems

Integrating TES systems with HVAC systems can provide enhanced cooling and/or heating in various applications e.g., commercial and residential buildings. TES systems are often categorized as heating TES and cooling TES (CTES). All TES systems incorporate a thermal energy storage material, a container for it and heat exchange equipment. TES storage media are generally chosen according to such parameters as thermal characteristics and capacity, availability, cost, durability and reliability.

### 3.2.1 Heating TES

In heating TES, heating capacity is obtained when available and used subsequently (e.g., seasonal storage systems which collect solar thermal energy during the summer for use in winter), or produced during off-peak hours when energy charges are lower than peak charges for subsequent peak-period use. Such systems usually are designed to provide space heating and/or domestic hot water (DHW). Various types of heating TES systems which can provide these heating loads exist, including sensible and latent types. Some examples of sensible heating TES systems follow (Dincer and Rosen, 2002):

- Concrete TES tanks
- Rock and water/rock TES
- Aquifer TES

These can often be thermally stratified, resulting in improved system efficiencies. Latent TES utilizes a phase change material (PCM) to store thermal energy. Typical PCMs are water, paraffins, eutectic salts and some polymers.

Thermochemical TES is receiving increasing interest, via research and feasibility studies, as an alternative type of TES which could increase the compactness of TES.

To better understand this value, it is useful to view it in the context of technical parameters for different types of TES systems. Various types of TES systems for a typical single-family house are compared in terms of storage density, TES volume, and useful life in Table 3.1, where compactness increases as storage density decreases.

**Table 3.1. Technical comparison of TES technologies.<sup>a</sup>**

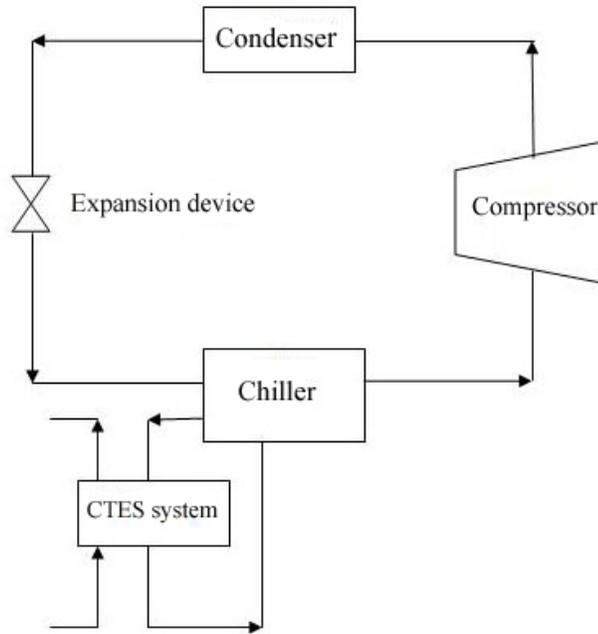
TES type	Energy storage density (GJ/m <sup>3</sup> )	Seasonal storage volume for single family house <sup>b</sup> (m <sup>3</sup> )	Useful life
Sensible	0.03-0.2 (0.03 for high-temp. oil, 0.1 for low-temp. oil)	120	Long (20 years for high- and low-temp. oil)
Latent (various salts)	0.3-0.5	60	10 <sup>2</sup> -10 <sup>3</sup> cycles
Thermochemical	0.4-3	6	N/A (depends on reactant degradation and side reactions)

<sup>a</sup> Adapted from several sources (Dincer and Rosen, 2002; van Helden, 2009, Bakker et al., 2009).

<sup>b</sup> Single family home is a residential building that can either be attached to another unit or stand separately. Generally, only one family at a time occupies a single family home. In 2005 in Northeast region of the U. S., the average single-family house completed had 2,334 square feet.  
(<http://www.eia.doe.gov/emeu/recs/recs2005/c&e/summary/pdf/tableus1part1.pdf>).

### 3.2.2 Cooling TES (CTES)

Cooling TES has systems store cooling capacity. The required cooling capacity is usually produced by at night periods and then used in the day. There are two main differences between conventional air conditioning system and cooling TES systems. First, required cooling loads in conventional air conditioning systems are supplied by removing heat with a working fluid (normally air or chilled water or a brine/antifreeze and water solution) while heat is removed in total or part using the storage medium in CTES systems. Second, conventional air conditioning systems operate in peak hours when cooling is required in a building while CTES systems operate during off-peak times when cooling is not required. The integration of TES in a conventional air conditioning system is illustrated in Figure 3.1.



**Figure 3.1. Integration of TES in a conventional air conditioning system.  
Adapted from Hussain et al. (2004).**

Electrical bills are usually dependant on electrical energy and electrical demand costs. Peak hours of energy consumption are usually in the day, and cooling TES can shift the operating period of electric air conditioning to the off-peak periods when both demand and usage are less than the peak period, lowering costs (Dincer and Rosen, 2002).

The storage medium is usually water-based in sensible CTES and eutectic salts (with phase change materials) in latent CTES systems. Sensible CTES systems account for most cold TES applications presently. Thermochemical TES may prove useful for cooling TES systems provided ongoing efforts to develop systems are successful.

The main TES storage media have different characteristics (Dincer and Rosen, 2002; Dincer, 2002):

1. Chilled water: As the sensible heat capacity of water is used to provide the required cooling, these systems have the largest storage tanks with the lowest storage densities, but they are the simplest in terms of equipment and operation. Factors which affect the volume of the storage tank are the temperature difference between the water supplied from the storage and the water supplying the load and the degree of separation between hot and cold water via thermal stratification in the storage tank. Water is a well understood and familiar medium. The operating temperature of these systems is between 3.3 and 5.5 °C, which is usually compatible with most conventional water chillers and distribution systems.
2. Ice: By using the latent heat of fusion of water to store cooling, these systems are smaller than chilled water systems for the same storage capacity. The required storage volume is commonly in the range of 0.07 to 0.09 cubic meters per ton-hour storage period (Pacific Gas and Electric Company, 1997). In terms of complexity and equipment installation, these systems are more complex than chilled water systems but more suitable when low temperatures are needed. The technologies used in this storage include ice harvesting, external ice-on coil, internal ice-on coil, encapsulated ice and ice slurry.
3. Eutectic salts: The characteristics of eutectic salt systems are often bracketed by those for the above systems. One difference is that the operating temperature of eutectic salts is higher than for the two other systems. PCMs that can undergo phase change at temperatures above 8.3 °C are suitable for this system. The storage capacity of PCMs is usually three times more than chilled-water systems and the net storage volume of

such a system is approximately 0.2 cubic meters per ton-hour of cooling (Pacific Gas and Electric Company, 1997).

The selection of a storage medium and TES system depend on various factors, as shown in Table 3.2.

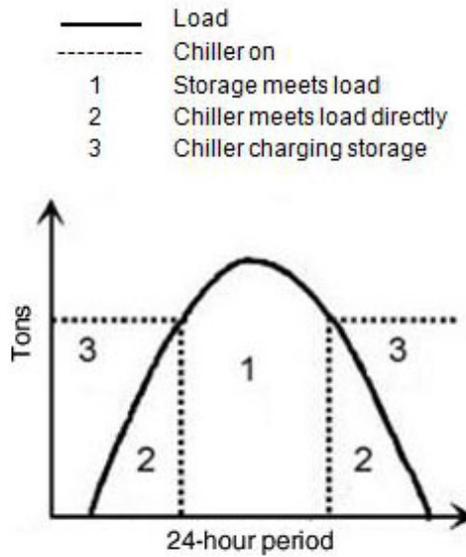
**Table 3.2. Comparison of different CTES systems.**

System	Suitable conditions for system	
	Space	Temperature
Chilled-water	Space is available	Moderately cool temperatures are needed
Ice	Space is limited	Low temperature are needed
Eutectic salt	Space is limited	Low temperatures are not required

### **3.2.3 Operating and Control Strategies for CTES**

CTES operating strategies are usually classified in two categories; full-storage and partial-storage, according to the cooling load transferred from peak periods.

A full-storage strategy (or complete load-shifting) shifts the entire peak cooling load to off-peak hours (see Figure 3.2). This system is usually operates at full capacity because it is designed for the hottest expected days and charges the storage during all off-peak hours. Thus, storage used in this system need large capacities. These systems are beneficial when peak demand costs are high and where there is a limited peak period.

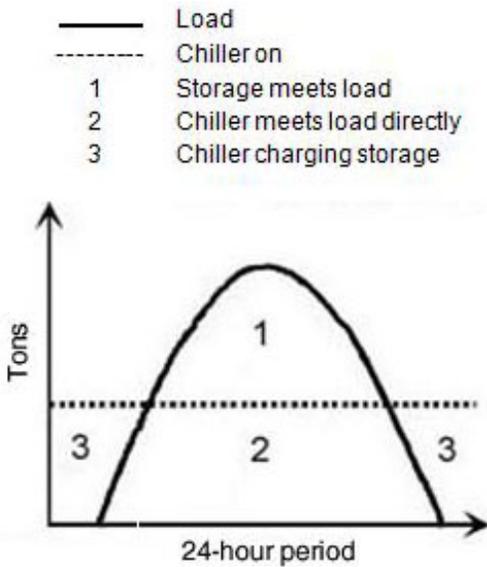


**Figure 3.2. Full-storage strategy. Adapted from Dorgan and Elleson (1994).**

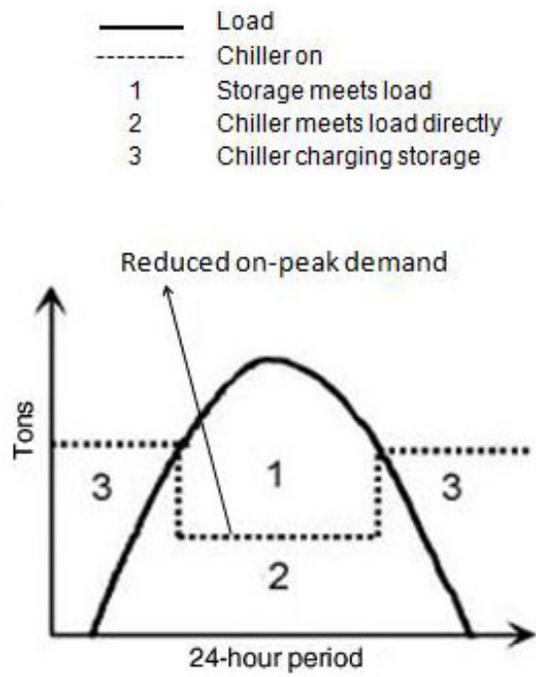
In a partial-load system, the chiller and storage both provide required cooling loads during peak periods. Such systems can be of two types:

- Load-levelling (see Figure 3.3): The chiller is selected to operate at its full capacity for 24 hours on the hottest days. This system is useful when peak cooling load greatly exceeds the average load.
- Demand-limiting (see Figure 3.4): The chiller operates at reduced capacity during peak hours.

Partial storage is often more advantageous economically than full storage because it involves lower initial costs, and the load-levelling strategy has lower costs relative to other options (demand-limiting and full-storage). Full-storage systems normally have the greatest costs. Much of the material in this section is based on the presentations of others (Dincer, 2002).



**Figure 3.3. Partial-storage, with a load-levelling strategy. Adapted from Dorgan and Elleson (1994).**



**Figure 3.4. Partial-storage strategy, with a demand-limiting strategy. Adapted from Dorgan and Elleson (1994).**

### 3.2.4 Feasibility Assessment and Advantages of CTES

Some important factors in selecting a CTES system follow (Dincer and Rosen, 2002):

- Design considerations, including storage strategy, chiller capacity, chiller efficiency, control system and economics.
- Technical specifications, including storage capacity, lifetime, safety, installation, environmental impacts, efficiency and sizing.

Advantages of CTES systems are as follows (Dincer, 2002; Hasnain and Alabbadi, 2000):

- A smaller refrigeration capacity is needed with CTES compared to conventional air conditioning systems because cooling loads are reduced during peak periods.
- Energy purchases with CTES systems are shifted to low-cost periods, reducing costs.
- Smaller equipment is needed with CTES systems (e.g., smaller piping, ducts, air handling unit, electrical equipment and pump) since less air circulation is needed. There is large air temperature-difference across the air handling unit.
- Refrigerant plants in CTES systems are more efficient relative to conventional ones because they usually operate at night when ambient temperatures are lower, allowing for cooler condenser temperatures and reducing energy use. In addition, the smaller pumps and fan use less energy.
- Chiller lifts are reduced.

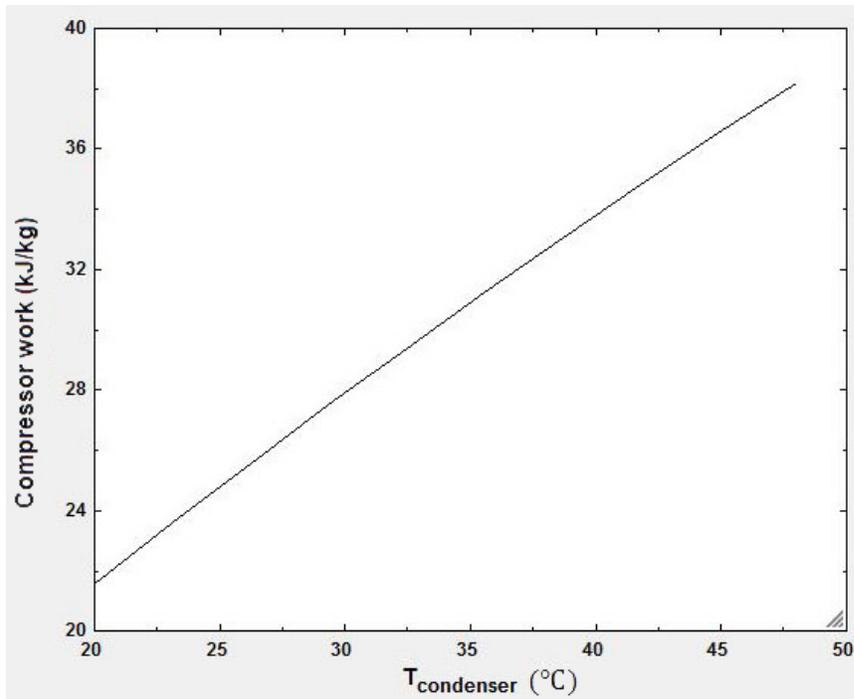
#### **3.2.4.1 CTES Effect on Chiller Lift**

According to ASHRAE Standard 90.1 (ASHRAE, 2007), chiller lift (or head pressure) can be expressed as

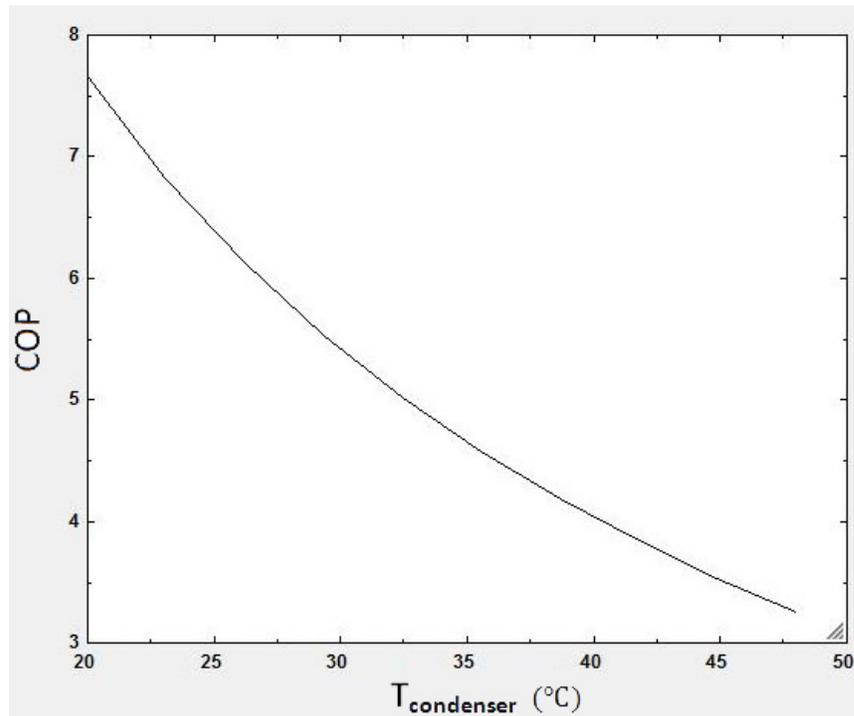
$$\text{Chiller lift} = \text{Entering condenser temperature} - \text{Leaving chilled water temperature} \quad (3.1)$$

Chiller lift also can be expressed as the difference between condenser refrigerant pressure and evaporator refrigerant pressure. Operating chillers at night reduces chiller lift because, in air-cooled condensers, the ambient dry bulb temperature is lower relative to daytime values. Lowering the chiller lift reduces compressor work, which is equal to the difference between enthalpy values at entering and exiting the compressor, and consequently energy consumption (Roth et al., 2006).

To illustrate this effect, a code has been written with Engineering Equation Solver (EES) to model a theoretical single-stage compression cycle. Thermodynamic constraints are adapted from Example 15.2 (McQuiston et al., 2005). The refrigerant is R134a and the condenser temperature is assumed to be 48 °C when the cycle operates during the day and there is no TES system. The condenser pressure is 1253 kPa and the evaporator pressure is 201 kPa. We investigate the effect of using TES system on the compressor work and cycle coefficient of performance (COP) (see Figures 3.5 and 3.6). When TES is incorporated, the chiller operates at night and the condensing temperature decreases. As condenser temperature is reduced, compressor work decreases and the cycle COP, increases. Therefore, the operating cost decreases with CTES because the compressor runs less than without TES.



**Figure 3.5. Variation of compressor specific work with condenser temperature.**



**Figure 3.6. Variation of cycle COP with condenser temperature.**

### **3.3 Case Studies**

Several case studies from various published studies are presented to illustrate the advantages of integrating TES with HVAC systems, considering both cooling TES and heating TES.

#### **3.3.1 Aquifer Thermal Energy Storage (ATES) for Air Conditioning of a Supermarket**

This HVAC system is designed for a supermarket building in the city of Mersin, Turkey. This HVAC system is integrated with aquifer thermal energy storage (ATES). The system uses groundwater from the aquifer to provide cooling loads and simultaneously stores waste heat in the aquifer. Thus this sensible TES can provide both space heating and cooling. In summer, the outside air temperature is between 30-35 °C while the groundwater temperature is around 18 °C at the same time. Cooling with groundwater decreases electricity use energy and the stored heat can be reused when needed in winter. The total energy that can be stored is 0.4 MWh. The integrated system is the first ATES application in Turkey and was launched in August 2001 with the cooling mode. The average system coefficient of performance (COP) is about 4.18, which is approximately 60% higher than a conventional system without TES. Much of the material in this section is based on the presentations of others (Paskoy et al., 2004).

### 3.3.1.1 System Description

The E20-II Hourly Analysis Program by Carrier Corporation was used to estimate the required annual heating and cooling loads, based on the following climate conditions and information:

- typical elevation: 6 m above the sea level
- 35 °C dry bulb and 29 °C wet bulb temperatures in the summer
- mean daily fluctuation in temperature of 7.4 °C
- winter design condition is 3 °C dry bulb temperature
- gross area for the building is 1800 m<sup>2</sup> and 1400 m<sup>2</sup> is to be air-conditioned

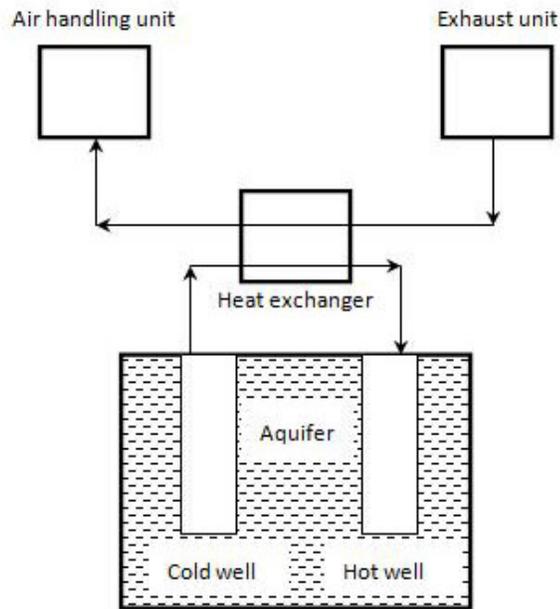
The peak load, corresponding to the hottest day in summer, was calculated as 195 kW and the required peak heating load, corresponding to the coldest day in summer, was calculated as 74 kW. The required heating and cooling loads for the supermarket are shown in Table 3.3.

**Table 3.3. Required heating and cooling load for a supermarket.\***

Cause of load	Cooling load (W)	Heating load (W)
Building components	36,800	34,800
Lighting	18,500	-
People	13,800	-
Ventilation	102,700	47,700

\* Source: Paskoy et al. (2004).

Two groups of wells are connected to the HVAC system, one for heating and another for cooling. A schematic of this system is depicted in Figure 3.7. Each well has a depth of 100 m and a casing diameter of 150 mm. The distance between the wells is 75 m.



**Figure 3.7. Schematic layout of the HVAC system integrated with ATEs.  
Adapted from Paskoy et al. (2004).**

The main components of this system are as follows:

- Four scroll compressors (Copeland ZR19M3)
- Two submersible pumps to extract groundwater from the wells (4 kg/s of groundwater is the design condition).
- High- and low-pressure switches, electric motor with over-heating and over-loading switches to protect compressors.
- A return air thermostat and high- and low-pressure sensors to control the capacity of the system.
- Reversing valve attached to compressors to provide the possibility for heat pump operation.
- Air handling unit to supply an air volume rate of 5500 l/s at 600 Pa external static pressure.

- Direct expansion heat exchanger (with aluminum fins and copper tubes) which can provide a total heat transfer area of 200 m<sup>2</sup> and a face velocity of 1.6 m/s.
- Exhaust unit with 2000 l/s air volume capacity and 350 Pa external static pressure.
- Fans for exhaust and air handling units connected to 1.5 kW and 7.5 kW electric motors, respectively.
- Stainless steel condenser with total condensing capacity of 200 kW at a 35 °C condensing temperature and 4 kg/s of water at 20 °C.

### **3.3.1.2 Results**

In order to compare energy consumption between the conventional HVAC system suitable for this supermarket and the ATES system, a typical conventional HVAC system (Mitsubishi DR101HEA packed type air-conditioner) has been selected as the reference system. The conventional system has the following conditions:

- Air cooled condenser with a cooling capacity of 31.8 kW at 35 °C outside air temperature.
- Average coefficient of performance of 2.67.

As mentioned before, the main difference between these two systems is that in the ATES system the heat is rejected to a low-temperature heat sink. The average temperature of the groundwater is around 18 °C which decreases electrical energy consumption for heat transfer, compared to a 30–35 °C outside air temperature. Table 3.4 compares cooling loads for the two systems for a summer day in 2001. The results show that the electricity consumption is reduced by 60% by integrating the conventional HVAC system with ATES.

**Table 3.4. Comparison of conventional HVAC and ATES systems.\***

Time	Temperature (°C)	Energy use rate (kW)		COP	
		Conventional	ATES	Conventional	ATES
09:00	29.7	59.41	40.15	2.77	4.10
12:00	33.3	72.26	45.91	2.68	4.21
15:00	35.0	74.16	45.17	2.59	4.21
18:00	33.4	70.07	44.44	2.66	4.19

\* Adapted from Paskoy et al. (2004).

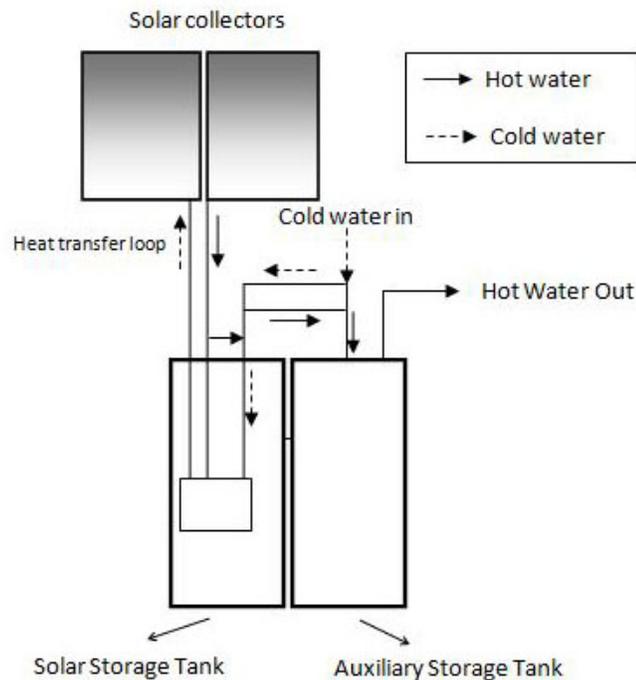
### **3.3.2 Drake Landing Solar Community (DLSC)**

The Drake Landing Solar Community (DLSC) is a collection of 52 single-detached homes located in Okotoks, Alberta. About 90 percent of required space heating loads (both space heating and water heating) are provided by solar thermal energy, making DLSC a good example of a sustainable energy system. As with many other seasonal TES applications, solar thermal energy is collected in the summer, stored underground, and recovered subsequently to heat the DLSC homes during winter. A sensible TES is used in the DLSC system (<http://www.dlsc.ca/index.htm>). The main components of the DLSC project are as follows:

- solar collector
- energy centre with short-term energy storage
- seasonal borehole thermal energy storage (BTES) system, which is an underground thermal storage
- district heating system
- energy efficient homes certified to the R-2000 Standard

### 3.3.2.1 System Description and Components

Each DLSC home is equipped with two solar panels installed on the roof of the home which are connected to a solar hot water tank in the basement. 60% of the required domestic hot water of each home is supplied by this system and when solar energy is not available, the hot water demand are provided by a natural gas system. The system is shown as Figure 3.8.



**Figure 3.8. Solar collector and domestic hot water system. Adapted from <http://www.dlsc.ca/index.htm>.**

The required solar energy is collected with an 800-panel garage mounted array. To smooth the process of capturing and storing of solar energy in the summer for heating in winter, seasonal and short-term thermal storage (STTS) are combined. The STTS tanks work as the central hub for dispatching heat between collectors, the district loop (DL), and the BTES. The district loop moves heat from the STTS to the houses.

### 3.3.2.2 Advantages of DLSC

The DLSC energy system has several advantages over conventional heating systems:

- DLSC is designed to supply approximately 90% of space heating in each home with solar energy, decreasing the community's dependence on fossil fuels notably.
- Greenhouse gas (GHG) emissions are reduced by about 5 tonnes annually, compared to the typical emissions is 6 to 7 tonnes of GHG per year for conventional Canadian houses.
- The system could be extendable for use in countries with cold climate where the sun shines infrequently during winter.
- DLSC is the largest subdivision of R-2000 standard single-family homes, which are 30% more efficient relative to conventional houses, in Canada.

Table 3.5 compares DLSC homes with typical homes in terms of energy savings and GHG emissions. It is seen in Table 3.5 that the Drake landing home uses  $6.1 + 9.6 = 15.7$  GJ of natural gas while a typical home uses  $100 + 26.5 = 126.5$  GJ of natural gas, leading to a savings of 110.8 GJ. The overall annual energy saving of 110.8 GJ leads to an annual GHG emission reduction of 5.65 tonnes.

**Table 3.5. Comparison of annual energy consumption for typical and Drake Landing homes.**

Resource	Space heating (GJ)		Water heating (GJ)	
	Typical home	Drake Landing home	Typical home	Drake Landing home
Natural gas	100	6.1	26.5	9.6
Solar	-	93.9	-	16.9

\* Adapted from <http://www.dlsc.ca/index.htm>.

### **3.3.2.3 Capturing Solar Energy**

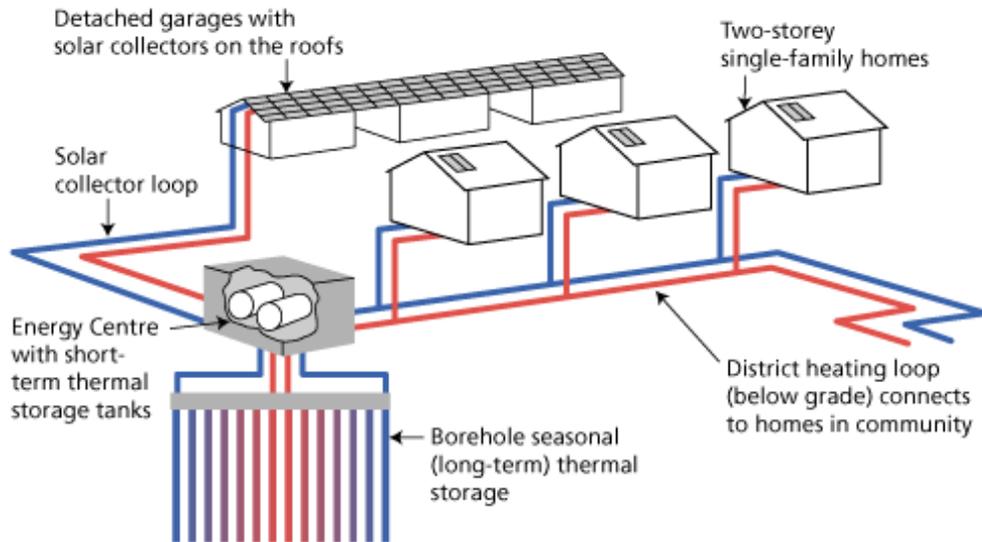
800 solar panels mounted on roofs of houses' garages produce 1.5 MW of thermal power during the charging period of this system in summer. The heat transfer fluid in the system is a glycol solution. This piping system is insulated to avoid heat losses during charging, storing and discharging. The working fluid is heated by solar energy via solar panels. The heated working fluid (glycol solution) travels along the roof of the building to absorb heat, down the end of the garage, and underground through a shallow underlying trench system, after which it reaches the heat exchanger in DLSC Energy Centre. There, heat is transferred to the water stored in a short-term storage tank and the glycol solution returns to the solar collector.

This system only starts working when the temperature in a component exceeds the temperature within a subsequent component. For instance, when the solar collectors absorb energy from the sun, the glycol temperature rises above the temperature of the water in the short-term storage tanks (STTS). Consequently, when the water temperature in the short-term storage tanks rises above the borehole thermal energy storage (BTES) temperature, the BTES pump start pumping to transfer heat from the STTS to the BTES and by this procedure, heat is transferred through the whole system. At night the collector pump shuts off but the BTES pump operates most of the night to provide stored energy.

### **3.3.2.4 Storing Solar Energy**

The heated water is distributed from the short-term storage tank to the BTES during summer, through a piping system. There are 144 boreholes extending 37 m below the ground over an area 35 m in diameter. Heat is transferred to the surrounding earth as the heated water passes through the piping system. The temperature of the earth can

reach 80 °C at the end of the summer season. The BTES is insulated by being covered with sand, high-density R-40 insulation, waterproof membrane, and landscaping materials. The water returns from the BTES to the short-term storage tanks in the Energy Centre to be heated again. The system is illustrated in Figures 3.9 and 3.10.



**Figure 3.9. Solar seasonal storage and district loop**  
(<http://www.dlsc.ca/index.htm>).

### 3.3.2.5 Distributing Solar Thermal Energy

During cold days in winter, heat is transferred from the BTES travels to the short-term storage tank in the Energy Centre and circulated to homes through a piping system comprising the district heating loop. A low-temperature air handler unit is located in the basement of each home, and a fan blows air across the warm fan coil, warming it and sending it for distribution via the home's ductwork. An automatic valve shuts the system when the temperature of the home's thermostat is met.

In the district heating system, the working fluid is water. All 52 houses are serviced by buried, pre-insulated piping. The district heating system is connected to the STTS through a heat exchanger in the Energy Centre. There are 4 individual

home-run loops off a manifold in the Energy Centre. The water temperature is modulated based on the outdoor temperature, and the flow is modulated based on the number of houses needing heat.

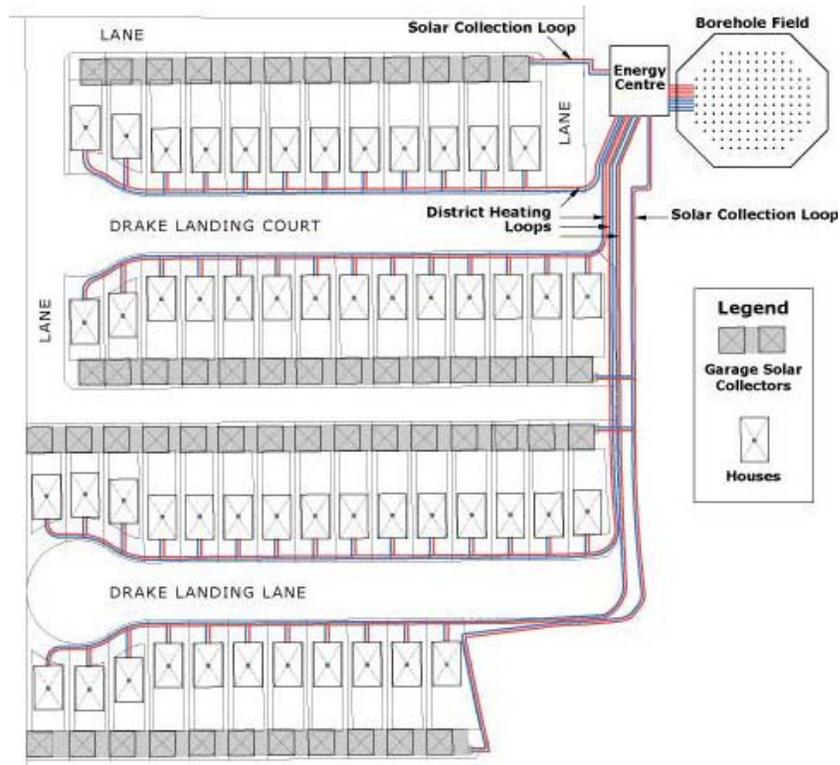
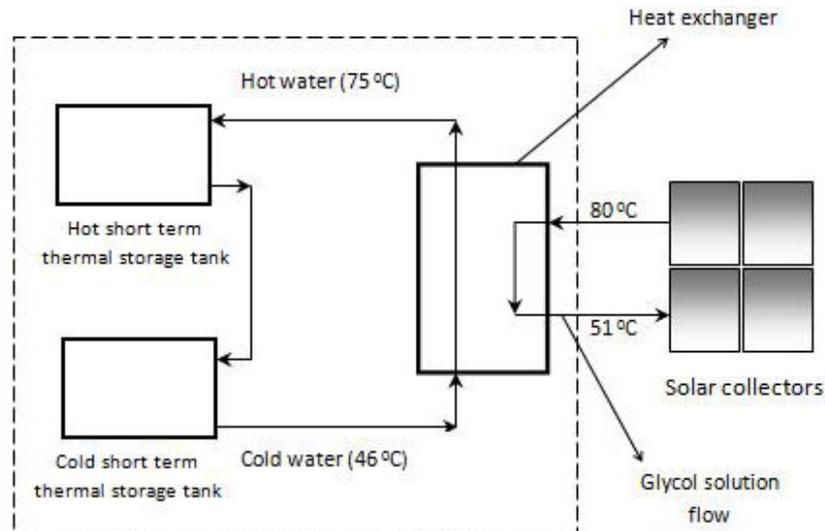


Figure 3.10. DLSC site plan (<http://www.dlsc.ca/index.htm>).

### 3.3.2.6 The Energy Centre

The Energy Centre area is 232 m<sup>2</sup>, and is the heart of the district heating system (Figure 3.11). It includes the short-term heat storage tanks, mechanical equipment such as pumps, expansion tanks, heat exchangers and controllers. Heat transfer for the solar collector loop, the borehole thermal energy storage loop and the district heating loop are done via the Energy Centre. Two horizontal, large water tanks are located in this space (occupying around 70% of the area of the Energy Centre). These tanks are

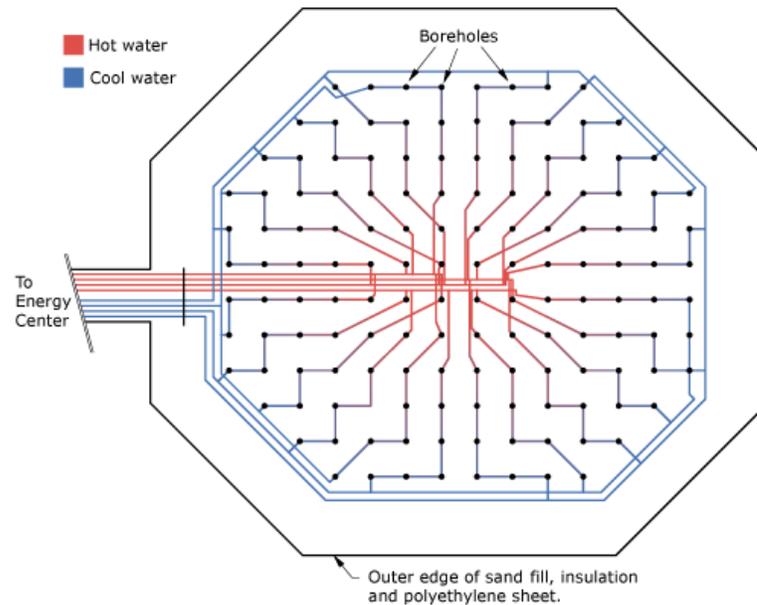
well-insulated and are 3.6 m diameter and 11 m long. For efficiency, the water temperatures within these tanks are stratified.



**Figure 3.11. DLSC energy centre, showing stratified short term thermal storage (STTS) tanks and solar collector loop. Adapted from <http://www.dlsc.ca/index.htm>.**

### **3.3.2.7 Borehole Thermal Energy Storage (BTES)**

In the BTES system, which is a large underground heat exchanger (Figure 3.12), heat collected during summer is stored for later utilization during winter. The tube in a single borehole has a “U” shape. To provide appropriate thermal contact with the surrounding soil, the borehole is filled with a thermally conducting grouting material. There are 144 boreholes, each of 150 mm diameter and 35 m deep spaced 2.25 m apart on centre. The piping is divided into four circuits and distributed through four quadrants.



**Figure 3.12. Aerial view of BTES at DLSC <http://www.dlsc.ca/index.htm>.**

### 3.3.3 Latent TES using PCM

This system is an example of utilizing PCM integrated with other systems to provide the heating and cooling loads of a power plant in Bromont, Quebec. IBM built the power plant in 1971 to achieve a 4% reduction in annual energy consumption which translates to a 500,000 MWh savings during 15 years of operation. The first plant included the following components:

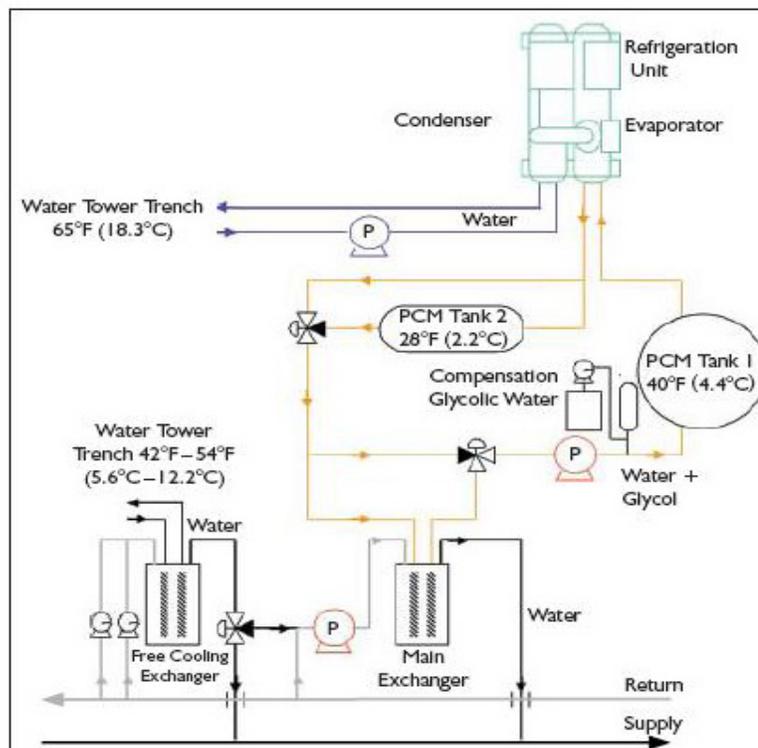
- six 1000 ton chillers, three of which used R-12 as a working fluid
- two 2000 ton chillers
- one 1000 ton natural cooling exchanger

According to a Quebec law since 1 Jan. 2006, any chiller running on R-12 was required to be decommissioned in the year following a repair. So, IBM modernized its plant by replacing the previous system with a new integrated system, including:

- one 1500 ton VFD (variable frequency drive) chiller,
- two 1600 ton-hour PCM thermal energy storage tanks, and

- one 2500 ton plate exchanger.

Artificial PCMs are used in this plant because they are suitable conductors relative to ice. There are 2 PCM storage tanks with different melting points,  $-2.2\text{ }^{\circ}\text{C}$  and  $4.4\text{ }^{\circ}\text{C}$  to improve efficiency. Ice expands during phase change from liquid to solid but artificial PCMs have negative expansion during this phase change and, as a result, do not put stress on the exchangers. The cooling medium in this system is a glycol-water mixture (25% glycol). Two TES tanks are installed in the loop; one above and one below the chiller. The upper storage tank is set at  $4.4\text{ }^{\circ}\text{C}$ , and regulates the chiller load and is always in operation. It can be unloaded/reloaded several times a day. The lower tank is set at  $-2.2\text{ }^{\circ}\text{C}$  and is used to support substantial long-term fluctuations. Used in bypass or line mode, it is loaded/unloaded one to two times a day. This system integrates the natural cooling exchanger (free cooling) that can be placed next to the TES system. A schematic of this system is shown in Figure 3.13.



**Figure 3.13. System operation schematic for latent TES system (Pare and Bilodeau, 2007).**

A partial-storage strategy is used, in which the system provides part of the peak load. The remaining demand is supplied by the TES. A load-levelling strategy is applied when peak demand is much greater than usual. Surplus energy is stored when demand is lower than the mechanical capacity and thermal storage provides the demand when demand exceeds the installed capacity. This approach reduces the size of the mechanical equipment. Much of the material in this section is based on the presentations of others (Pare and Bilodeau, 2007).

Some advantages of this integrated system are as follows:

- no maintenance required for PCMs, which are contained in a sealed tank
- 50% reduction in refrigerant requirements
- 45% reduction in GHG emissions for chilled water production
- 6% annual energy saving (5,300 MWh) relative to the previous application
- reduced electrical power consumption (more than 1 MW annually)

### **3.3.4 Solar Heating and Cooling by a Thermochemical Process**

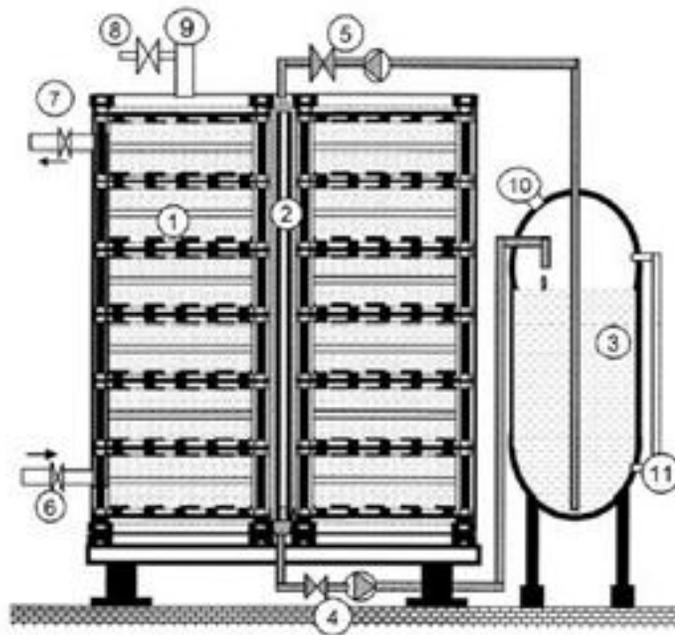
In this system, a chemical heat pump, which uses chemical reactions driven by thermal solar energy, provides heating and cooling with a compact TES system (Figure 3.14). This prototype can provide heating and cooling of 60 kWh (in 84 hours) and 40 kWh (in 62 hours), respectively. The reactor of this system has 1 m<sup>3</sup> volume. The primary advantages of thermochemical TES is its compactness relative to other types of TES, due to the higher energy density of thermochemical storage.

This system is based on the integration of a flat plate solar collector and a chemical (solid/gas sorption) process using bromide strontium as the reactant and water as the working fluid in a closed TES system. This TES enables a high energy density relative to other types of TES systems as well as the possibility of energy

storage without large losses. The system is intended to provide heating and cooling storage functions to facilitate direct floor heating and cooling. The storage reaction can be expressed as follows:



This system is comprised of two heat transfer loops, one between a plate-type heat exchanger and solar panels, and another between the heat exchanger and the floor of the building. The maximum output temperature of the solar panel is 80 °C and, while heating inlet of the floor in mid seasons is 35 °C and in summer is 18 °C. Much of the material in this section is based on the presentations of others (Mauran et al., 2008).



**Figure 3.14. Schematic of a prototype thermochemical TES (Mauran et al., 2008); (1) Module (2) Evaporator/condenser (3) Reactive water stored in water tank (4, 5) Pouring water (6, 7) Collector inlet and outlet (8) Vacuum valve for coolant of exchanger plates (9) Pressure level (10) Liquid level (11) Measures.**

# Chapter 4

## Energy and Exergy Analysis of a Closed Thermochemical Energy Storage System

### 4.1 Introduction

In this chapter, energy and exergy analyses are carried out for a general closed thermochemical TES system and its charging, storing and discharging processes. The objective is to improve understanding and thereby support development and ultimate implementation of thermochemical TES technology. An illustrative example is included based on experimental data from the open literature.

### 4.2 Energy and Exergy Analyses

A general thermochemical TES is considered and energy and exergy analyses are performed. Efficiencies are determined, and the charging, storing and discharging processes examined.

This system considered consists of a working fluid and a thermochemical material. Energy from an energy resource (e.g., solar energy collected via a solar thermal collector) is transferred to a working fluid. This thermal energy provides the necessary energy for dissociation of the thermochemical material. After a storing period, energy released from synthesis of thermochemical material is absorbed by the working fluid for heating purposes (e.g., domestic hot water heating, space heating).

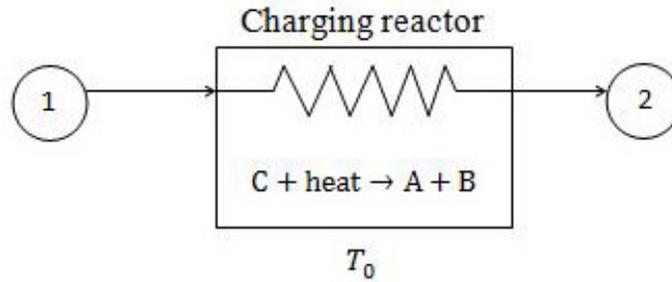
The following assumptions made in this investigation:

- Chemical reactions within the reactor occur at constant pressure.

- Work interactions into and out of the control volume are neglected, as are kinetic and potential energy. The former assumption implies that pump, compressor and fan work is neglected.
- In the charging process, the initial temperature of the thermochemical material is assumed to be that of the reference environment  $T_0$ .
- There are no energy losses during the storing period and thermochemical materials are stored at the reference-environment temperature.
- The physical exergy change of the components is neglected relative to their chemical exergy changes.

#### 4.2.1 Charging Process

A general charging process for a thermochemical TES is illustrated in Figure 4.1. In this system, the analysis is limited to closed TES systems where internal substances are separate from the heat transport fluid. The required temperature for dissociation of the thermochemical material is denoted  $T_s$  and the initial temperature of thermochemical material is that of the reference environment  $T_0$ . The temperature  $T_1$  is supplied by the energy resource (e.g. solar thermal collection panels) and  $T_2$  is the outlet temperature of the charging reactor. In this system, the working or heat transport fluid (labeled 1 and 2 in Figure 4.1) is separate from materials A, B and C. The thermochemical TES medium changes during charging from material C at the start of the process to materials A and B after the dissociation reaction occurs.



**Figure 4.1. Charging process in thermochemical TES. The heat transport fluid used for charging the TES enters at state 1 and exits at state 2.**

#### 4.2.1.1 Energy Analysis for Charging

A general energy balance for this system can be written as (Dincer and Rosen, 2002):

$$\text{Energy input} - \text{Energy output} = \text{Energy accumulation} \quad (4.1)$$

The net input energy supplied by the working fluid can be evaluated with an energy balance as follows:

$$Q_{input} = m_c C_p (T_1 - T_2) \quad (4.2)$$

Here,  $m_c$  and  $C_p$  are the mass and specific heat at constant pressure of the working fluid, and  $T_2$  and  $T_1$  are the final and initial temperatures of the working fluid.

The charging process includes three steps. The first step is preheating the thermochemical material from its initial temperature to the dissociation temperature  $T_s$ . This heat requirement can be evaluated as follows:

$$Q_{preheat} = M C_{ps} (T_s - T_0) \quad (4.3)$$

Here,  $M$  and  $C_{ps}$  denote mass and specific heat at constant pressure of the thermochemical storage material.

The second step is the thermochemical reaction in which the energy of the thermochemical material increases by an amount equivalent to the enthalpy of reaction  $\Delta H$ .

The third step involves cooling after the reaction from the reaction temperature to the reference-environment temperature, which is the temperature at which it is assumed the thermochemical materials are stored. This heat addition term is negative, indicating heat is removed. This heat interaction may be treated as a loss, but it differs from other miscellaneous heat losses. The heat removed during cooling can be expressed as

$$Q_{cooling} = \dot{M}C'_{ps}(T_0 - T_s) \quad (4.4)$$

Here,  $\dot{M}$  and  $C'_{ps}$  are the mass and specific heat at constant pressure of the thermochemical products (after the separation reaction).

The heat interactions  $Q_{cooling}$  and  $Q_{preheat}$  can be treated as part of total heat loss during the charging process. Therefore, an energy balance for the charging process, accounting for the net heat input and the accumulation of energy in the storage material, as well as the heat loss  $Q_{loss}$ , can be written as follows:

$$Net\ energy\ input - Heat\ loss = Energy\ accumulation\ in\ TES \quad (4.5)$$

or

$$m_c C_p (T_1 - T_2) - Q_{loss} = \Delta H_{reaction} \quad (4.6)$$

where  $Q_{loss}$  denotes the total heat loss, which can be expressed as follows:

$$Q_{loss} = Q'_{loss} + (Q_{cooling} - Q_{preheat}) \quad (4.7)$$

Thus, we can write

$$m_c C_p (T_1 - T_2) - [Q'_{loss} + (Q_{cooling} - Q_{preheat})] = \Delta H_{reaction} \quad (4.8)$$

Here, the total heat loss for the charging process is expressed in terms of the heat transfer between the reactants and the reactor surface  $Q'_{loss}$  (Darkwa, 1998) as well as the net cooling loss  $(Q_{cooling} - Q_{preheat})$  before and after the dissociation reaction.

The energy efficiency of the charging process can consequently be expressed as follows:

$$\eta_c = \frac{\text{Energy gained by thermochemical material}}{\text{Energy input}} \quad (4.9)$$

or

$$\eta_c = \frac{\Delta H_{\text{reaction}}}{m_c c_p (T_1 - T_2)} \quad (4.10)$$

### 4.2.1.2 Exergy Analysis for Charging

A general exergy balance for this system can be written as

$$\text{Exergy input} - \text{Exergy output} - \text{Exergy consumption} = \text{Exergy accumulation} \quad (4.11)$$

The exergy balance, which is based mainly on the second law of thermodynamics, can be written for this system as follows:

$$\text{Exergy input} - \text{Exergy loss} - \text{Exergy destruction} = \text{Exergy accumulation} \quad (4.12)$$

Here, the exergy input can be calculated as

$$\text{Net exergy delivered by charging fluid} = m_c [h_1 - h_2 - T_0 (s_1 - s_2)] \quad (4.13)$$

Note that the exergy destruction is proportional to entropy generation due to irreversibilities. Therefore,

$$m_c [h_1 - h_2 - T_0 (s_1 - s_2)] - \epsilon_D - [\epsilon'_{\text{loss}} + (\epsilon_{\text{cooling}} - \epsilon_{\text{preheat}})] = \Delta \epsilon_{\text{reaction}} \quad (4.14)$$

where  $h_1$  and  $h_2$  denote the specific enthalpy of the charging fluid at the input and output conditions,  $s_1$  and  $s_2$  denote the specific entropy of the charging fluid at the input and output conditions. Also,  $\epsilon_D$  denotes the exergy destruction,  $\Delta \epsilon_{\text{reaction}}$  the exergy accumulation in the charging process and  $T_0$  the reference temperature.

#### 4.2.1.2.1 Evaluation of Exergy Accumulation during Reaction

To determine the exergy change during a thermochemical reaction  $\Delta \epsilon_{\text{reaction}}$ , we calculate the exergy of reactants before the reaction as well as the exergy of products

after the reaction. The difference between these two quantities is the exergy change within the control volume over the period of the reaction.

The exergy of the control volume before the reaction is the sum of the exergies of the reactants. This exergy includes the physical, potential, kinetic and chemical exergy components of the reactants. As pointed out earlier, potential and kinetic exergy are neglected. Consequently, potential and kinetic exergy can be neglected and we need only focus on the physical and chemical exergy of the reactants.

The chemical exergy of compounds can be determined following the treatment (Szargut, 1980, 1989). The standard chemical exergy of a chemical compound  $\epsilon_{chn}$  can be calculated by means of the exergy balance for a reversible reaction:

$$\epsilon_{chn} = \Delta G_f + \sum_e n_e \epsilon_{chne} \quad (4.15)$$

Here,  $\Delta G_f$  denotes the Gibbs energy of formation,  $n_e$  denotes the amount of element e (in kmol), and  $\epsilon_{chne}$  denotes the standard chemical exergy of the element.

The physical exergy of a compound can be evaluated as follows (Bejan, 2006):

$$\epsilon_{ph} = m[(h - h_0) - T_0(s - s_0)] \quad (4.16)$$

where  $h_0$  and  $s_0$  denote the specific enthalpy and the specific entropy of the charging fluid at the reference environment, respectively. We can thus determine the total exergy of reactants as

$$\epsilon_{tot,reactants} = (\epsilon_{ch})_{reactants} + (\epsilon_{ph})_{reactants} \quad (4.17)$$

and of products as

$$\epsilon_{tot,products} = (\epsilon_{ch})_{products} + (\epsilon_{ph})_{products} \quad (4.18)$$

The exergy change (exergy accumulation) associated with the reaction can be evaluated as

$$\Delta \epsilon_{reaction} = \epsilon_{tot,products} - \epsilon_{tot,reactants} \quad (4.19)$$

We can evaluate the exergy efficiency of the charging process as follows:

$$\psi_c = \frac{\text{Exergy stored in reaction}}{\text{Exergy input}} = \frac{\Delta \epsilon_{\text{reaction}}}{m_c[h_1 - h_2 - T_0(s_1 - s_2)]} \quad (4.20)$$

or

$$\psi_c = \frac{\epsilon_{\text{tot,products}} - \epsilon_{\text{tot,reactants}}}{m_c[h_1 - h_2 - T_0(s_1 - s_2)]} \quad (4.21)$$

## 4.2.2 Storing Process

According to the assumptions made for the storing process, energy and exergy analysis are performed.

### 4.2.2.1 Energy Analysis and Efficiency for Storing

An energy balance for the storing process can be expressed as (Dincer and Rosen, 2002)

$$-\text{Energy loss} = \text{Energy accumulation} \quad (4.22)$$

It can be assumed that there are no energy losses during the storing period. Therefore, the energy accumulation is equal to zero. The energy efficiency of storing period can thus be written as

$$\eta_s = \frac{\text{Energy accumulation in TES during charging and storing}}{\text{Energy accumulation in TES during charging}} \quad (4.23)$$

According to the assumption, the energy efficiency of the storing process is equal to unity.

### 4.2.2.2 Exergy Analysis and Efficiency for Storing

An exergy balance for the storing process can be expressed as

$$-\text{Exergy loss} - \text{Exergy consumption} = \text{Exergy accumulation} \quad (4.24)$$

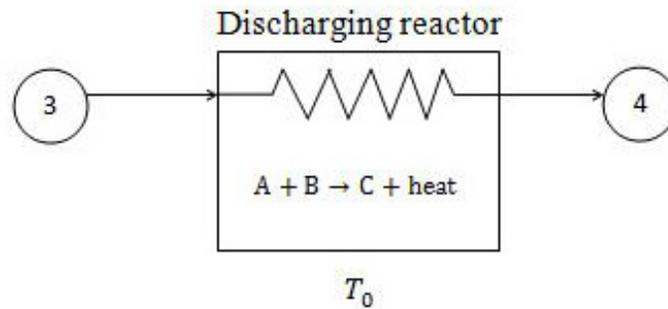
The exergy efficiency of the storing period can be written as

$$\psi_s = \frac{\text{Exergy accumulation in TES during charging and storing}}{\text{Exergy accumulation in TES during charging}} \quad (4.25)$$

For the assumptions considered for storing, the exergy loss and exergy consumption are equal to zero and the exergy accumulation is equal to zero. Also, the exergy efficiency of the storing process is equal to unity.

### 4.2.3 Discharging Process

A general discharging process for a thermochemical TES is illustrated in Figure 4.2. In this process, components A and B, which have been stored separately, are combined, allowing the discharging reaction to occur. The energy released by this exothermic reaction can be recovered by a working fluid in a closed TES system. The working fluid enters the reactor at  $T_3$  and exits at  $T_4$ .



**Figure 4.2. Discharging process in thermochemical TES. The heat transport fluid used for discharging the TES enters at state 3 and exits at state 4.**

#### 4.2.3.1 Energy Analysis for Discharging

The net input energy is equal to the energy released by the reaction (enthalpy of formation). We can write an energy balance for this process as follows (Dincer and Rosen, 2002):

$$-[\text{Energy recovered} + \text{Heat Loss}] = \text{Energy accumulation} \quad (4.26)$$

where the energy accumulation is a negative value equivalent to the energy released during the exothermic reaction. This energy recovered by the working fluid can be calculated as follows:

$$Q_{recovered} = m_d C_p (T_4 - T_3) \quad (4.27)$$

We can evaluate energy efficiency of this process as follows:

$$\eta_d = \frac{\text{Energy recovered}}{\text{Energy released in reaction}} = \frac{\text{Energy increase of charging fluid}}{\text{Energy released in reaction}} \quad (4.28)$$

or

$$\eta_d = \frac{m_d C_p (T_4 - T_3)}{\Delta H_{reaction}} \quad (4.29)$$

### 4.2.3.2 Exergy Analysis for Discharging

We can write an exergy balance for the discharging process as follows:

$$-(\text{Exergy recovered} + \text{Exergy loss}) - \text{Exergy destruction} = \text{Exergy accumulation} \quad (4.30)$$

The first term in this expression (exergy recovered) can be evaluated as

$$\text{Exergy of charging fluid} = m_d [h_4 - h_3 - T_0 (s_4 - s_3)] \quad (4.31)$$

where  $m_d$  is the mass flow for the working fluid and  $h_3, h_4, T_3$  and  $T_4$  are its properties.

We can evaluate the exergy efficiency of this process as

$$\psi_d = \frac{\text{Exergy recovered}}{\text{Exergy released in reaction}} = \frac{\text{Exergy increase of charging fluid}}{\text{Exergy released in reaction}} \quad (4.32)$$

or

$$\psi_d = \frac{m_d [h_4 - h_3 - T_0 (s_4 - s_3)]}{\epsilon_{tot, products} - \epsilon_{tot, reactants}} \quad (4.33)$$

The exergy change of the thermochemical storage material  $\Delta \epsilon_{reaction}$  can be evaluated following the same process used for the charging process.

#### 4.2.4 Overall TES Process

Using the same methodology, energy and exergy analysis of the overall TES process are performed.

##### 4.2.4.1 Energy Analysis and Efficiency for Overall Process

An energy balance for the overall storage process can be written as

$$\text{Energy input} - (\text{Energy recovered} + \text{Heat loss}) = \text{Energy accumulation} \quad (4.34)$$

or

$$m_c C_p (T_1 - T_2) - m_d C_p (T_4 - T_3) - Q_{loss,tot} = \Delta E \quad (4.35)$$

where  $\Delta E$  denotes the energy accumulation, given as the difference between the initial and the final energy contents of the storage, and  $Q_{loss,tot}$  represents the total heat loss during the process (charging, storing and discharging). For the case of a complete cycle with identical initial and final states,  $\Delta E = 0$  and the overall energy balance simplifies.

The energy efficiency for the overall storage process can be written as follows:

$$\eta_o = \frac{\text{Energy recovered from TES during discharging}}{\text{Energy input to TES during charging}} \quad (4.36)$$

or

$$\eta_o = \frac{m_d C_p (T_4 - T_3)}{m_c C_p (T_1 - T_2)} \quad (4.37)$$

##### 4.2.4.2 Exergy Analysis and Efficiency for Overall Process

Similarly, an exergy balance for the overall storage process can be written as

$$\text{Exergy input} - [\text{Exergy recovered} + \text{Exergy loss}] - \text{Exergy destruction} = \text{Exergy accumulation} \quad (4.38)$$

or

$$m_c[h_1 - h_2 - T_0(s_1 - s_2)] - m_d[h_4 - h_3 - T_0(s_4 - s_3)] - \epsilon_{loss,tot} - \epsilon_{D,tot} = \Delta\epsilon \quad (4.39)$$

Here,  $\epsilon_{loss,tot}$  and  $\epsilon_{D,tot}$  denote the total exergy loss and the total exergy destruction during the overall TES process, accounting for charging, storing and discharging. Exergy losses are related to heat losses during each process. The exergy accumulation  $\Delta\epsilon$  is the difference between the initial and the final exergy contents of the storage. For the case of a complete cycle with identical initial and final states,  $\Delta\epsilon = 0$  and the overall exergy balance simplifies.

The exergy efficiency for the overall storage process can be expressed as follows:

$$\psi_o = \frac{\text{Exergy recovered from TES during discharging}}{\text{Exergy input to TES during charging}} \quad (4.40)$$

or

$$\psi_o = \frac{m_d[h_4 - h_3 - T_0(s_4 - s_3)]}{m_c[h_1 - h_2 - T_0(s_1 - s_2)]} \quad (4.41)$$

## 4.4 Illustrative Example

To illustrate the analysis and efficiencies of a thermochemical TES system, an existing system is considered for which experimental data have been reported (Mauran et al., 2008). This system has been introduced earlier in the section 3.3.4.

### 4.4.1 System Description

This illustrative example is based on the integration of a flat plate solar collector and a chemical (solid/gas sorption) process using bromide strontium as the reactant and water as the working fluid in a closed TES system. This TES enables a high energy density relative to other types of TES systems as well as the possibility of energy

storage without large losses. The system is intended to provide heating and cooling storage functions to facilitate direct floor heating and cooling. The storage reaction can be expressed as follows:



In this reaction,  $\text{SrBr}_2 \cdot \text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  are porous solid matrices and  $\text{H}_2\text{O}$  is in the vapor phase. We have selected data for the heating operation (floor heating) during the mid seasons of Fall and Spring.

The system is comprised of two heat transfer loops. The first heat transfer loop is between a plate-type heat exchanger and solar panels, and the second is between the heat exchanger and the floor of the building. The mass of  $\text{SrBr}_2 \cdot \text{H}_2\text{O}$  is 171.3 kg and the mass of exchanged water in the reactor is 57.9 kg. The water (working fluid) flows at a rate of 6 l/min.

The thermodynamic constraints for the reactive pair and for mid-season conditions are as follows:

- Maximum output temperature of the flat-plate solar collector = 80 °C
- Temperature of the external environment = 7 °C
- Inlet temperature for floor heating = 35 °C
- Solid/gas equilibrium temperature for the dehydration phase = 43 °C
- Solid/gas equilibrium temperature for the hydration phase = 43 °C

The total volume of the prototype reactor is 1 m<sup>3</sup> and the system is able to store 60 kWh for the heating function.

## 4.4.2 Energy Analysis of TES Processes

The energy efficiencies are determined for the charging and discharging processes for the considered thermochemical TES, as well as for the overall process. Note that the energy efficiency for the storing period is not discussed extensively, as it is 100%.

### 4.4.2.1 Charging Process

The charging energy efficiency is calculated using Equation (4.10). The solid/gas reaction is



According to (Mauran et al., 2008), the dehydration cycle occurs over 42 hours. The energy efficiency of the charging process (i.e., dehydration) can be evaluated with the following data, which are obtained using Engineering Equation Solver (EES) software:

- Water input temperature,  $T_1 = 70 \text{ }^\circ\text{C}$
- Water output temperature,  $T_2 = 50 \text{ }^\circ\text{C}$
- $\rho_c = 983.2 \text{ kg/m}^3$  (at the mean temperature of the inlet and outlet conditions of the working fluid,  $T_{mean} = (T_1 + T_2)/2 = 60 \text{ }^\circ\text{C}$ )
- $C_p = 4.183 \text{ kJ/kg K}$  (at the mean temperature of the inlet and outlet conditions of the working fluid)
- Nominal flow of pouring water (working fluid) = 6 l/min
- $m_c = \rho_c V_c = (983.2 \text{ kg/m}^3 \times 10^{-3} \text{ l/m}^3) \times (6 \text{ l/min} \times 60 \text{ min/hour} \times 42 \text{ hour}) = 14,866 \text{ kg}$
- Mass of water as product = 57.9 kg
- Dehydration duration = 42 hours

For this illustrative example, the value of  $\Delta H_{reaction}$  is the enthalpy of separation reaction which is equal to 3,732 kJ/kg H<sub>2</sub>O. But there is 57.9 kg water in this closed loop system, so the enthalpy of the charging reaction regarding the number of moles of water (5 moles) can be evaluated as the numerator of the Equation (4.10) as

$$\Delta H_{reaction} = (5 \times 3,732 \text{ kJ/kg H}_2\text{O} \times 57.9 \text{ kg H}_2\text{O}) = 1,080,414 \text{ kJ} \quad (4.44)$$

The net energy input to the system during the charging process can be determined by calculating the mass of the working fluid ( $m_c$ ) during the charging process which has been calculated earlier as 14,866 kg. The temperature difference and  $C_p$  are known. So,

$$Q_{input} = 14,866 \text{ kg} \times 4.183 \text{ kJ/kg K} \times (70 - 50)\text{K} = 1,243,689 \text{ kJ} \quad (4.45)$$

Thus the energy efficiency of the dehydration process becomes

$$\eta_c = \frac{1,080,414}{1,243,689} = 0.86 \quad (4.46)$$

#### 4.4.2.2 Discharging Process

The energy efficiency of the discharging process (i.e., hydration) can be calculated using  $\Delta H_{reaction}$  of the reaction and the expression for energy efficiency given by Equation (4.29). The solid/gas reaction is:



The energy efficiency of the discharging process (i.e., hydration) can be evaluated with the following data:

- Water input temperature,  $T_3 = 25 \text{ }^\circ\text{C}$
- Water output temperature,  $T_4 = 35 \text{ }^\circ\text{C}$

- $\rho_d = 995.7 \text{ kg/m}^3$  (at the mean temperature of the inlet and outlet conditions of the working fluid,  $T_{mean} = (T_3 + T_4)/2 = 30 \text{ }^\circ\text{C}$ )
- $C_p = 4.183 \text{ kJ/kg K}$  (at the mean temperature of the inlet and outlet conditions of the working fluid)
- Nominal flow of pouring water (working fluid)= 6 l/min
- $m_d = \rho_d V_d = (995.7 \text{ kg/m}^3 \times 10^{-3} \text{ l/m}^3) \times (6 \text{ l/min} \times 60 \text{ min/hour} \times 42 \text{ hour}) = 15,055 \text{ kg}$
- Mass of water as reactant (component B) = 57.9 kg
- Hydration duration = 42 hours

In this discharging energy efficiency expression, the numerator is the net energy output from the discharging reaction, which can be calculated using the same method as employed for charging. The total mass of the working fluid is equal to 15,055 kg and the temperature difference and  $C_p$  and the temperature are known. So,

$$Q_{recovered} = 15,055 \text{ kg} \times 4.183 \text{ kJ/kg K} \times (35 - 25)\text{K} = 629,750 \text{ kJ} \quad (4.48)$$

The denominator is the value of  $\Delta H_{reaction}$  for the solid/gas reaction. The energy efficiency of the hydration process can therefore be evaluated as follows:

$$\eta_d = \frac{629,750}{1,080,414} = 0.58 \quad (4.49)$$

#### 4.4.3 Exergy Analysis of TES Processes

Charging, discharging and overall exergy efficiencies are determined for the considered thermochemical TES. As before, the exergy efficiency for the storing period (100%) is not discussed extensively.

### 4.4.3.1 Charging Process

The exergy efficiency of the charging process can be evaluated by using Equation (4.21). According to the inlet and outlet conditions of the working fluid (water), the relevant properties are as follows:

- $h_1 = 293.1$  kJ/kg (at  $T_1 = 70$  °C,  $P_1 = 101$  kPa)
- $s_1 = 0.9549$  kJ/kg K (at  $T_1 = 70$  °C,  $P_1 = 101$  kPa)
- $h_2 = 209.4$  kJ/kg (at  $T_2 = 50$  °C,  $P_2 = 101$  kPa)
- $s_2 = 0.7037$  kJ/kg K (at  $T_2 = 50$  °C,  $P_2 = 101$  kPa)

As mentioned earlier, in calculating the exergy values for the products and reactants, the physical exergy change of the components can often be neglected relative to their chemical exergy changes. This assumption is applied in this analysis. The standard chemical exergy of components can be evaluated using Equation (4.15). A methodology of calculating the standard chemical exergy of components is described by Szargut (1989) for normal reference-environment conditions ( $T_0 = 298.15$  K;  $P_0 = 0.101325$  MPa). Here, the compounds considered are SrBr<sub>2</sub> and H<sub>2</sub>O, and the standard chemical exergy values are determined as shown in Table 4.1.

**Table 4.1. Standard chemical exergy of selected components.**

Compound	$\Delta G_f^*$ (kJ/mol)	$n_e$		$\epsilon_{chne}$ (kJ/mol)		$\epsilon_{chn}$ (kJ/mol)
SrBr <sub>2</sub>	-697.1	1 (Sr)	1 (Br <sub>2</sub> )	749.8 (Sr)	101.2 (Br <sub>2</sub> )	153.9
H <sub>2</sub> O (gas)	-228.75	1 (H <sub>2</sub> )	0.5 (O <sub>2</sub> )	236.09 (H <sub>2</sub> )	3.97 (O <sub>2</sub> )	9.33
H <sub>2</sub> O (liquid)	-237.32	1 (H <sub>2</sub> )	0.5 (O <sub>2</sub> )	236.09 (H <sub>2</sub> )	3.97 (O <sub>2</sub> )	0.76

\* Taken from Woods and Garrels (1987)

In this example there are 171.3 kg of  $\text{SrBr}_2 \cdot \text{H}_2\text{O}$  and, according to a mass balance for the system, 229.2 kg of  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ . With the molecular weights of the components we can calculate the number of moles for each component (see Table 4.2). In calculating the standard chemical exergy of reactants and products, we can evaluate  $\Delta G_f$  for  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot \text{H}_2\text{O}$  as the sum of  $\Delta G_f$  for  $\text{SrBr}_2$  and six times and one time that of liquid water, respectively, and follow the same methodology. For  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ , for instance,

$$\epsilon_{chn} = [-697.1 + (-237.32 \times 6)] + [(749.8 + 101.2) + 6 \times (236.09 + 3.97/2)] = 158.43 \text{ kJ/mol} \quad (4.50)$$

**Table 4.2. Standard chemical exergy of selected components.**

Component	Molecular weight (g)	Mass (kg)	Number of moles	Standard chemical exergy (kJ/mol)
$\text{SrBr}_2 \cdot \text{H}_2\text{O}$	265.44	171.3	645	154.65
$\text{H}_2\text{O}$ (gas)	18.01	57.9	3198	9.33
$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	355.49	229.2	645	158.43

In order to calculate the charging exergy efficiency, the numerator of Equation (4.21) denotes the difference between the standard chemical exergy of products and reactants. In the charging reaction,  $\text{SrBr}_2 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  are products of the reaction and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  is the reactant. The standard chemical exergy of each of the components and their corresponding number of moles are evaluated and shown in Table 4.2. So,

$$\Delta \epsilon_{reaction} = [(645 \text{ mol} \times 154.65 \text{ kJ/mol}) + (3198 \text{ mol} \times 9.33 \text{ kJ/mol})] - (645 \text{ mol} \times 158.43 \text{ kJ/mol}) = 27,399 \text{ kJ} \quad (4.51)$$

For the denominator of the fraction, the total mass of the working fluid has been evaluated before and other required properties of the working fluid (enthalpy and entropy) are known as well. Therefore,

$$\epsilon_{input} = 14,866 \text{ kg} \times (293.1 \text{ kJ/kg} - 209.4 \text{ kJ/kg} - 298 \text{ K} \times (0.9549 \text{ kJ/kg K} - 0.7037 \text{ kJ/kg K})) = 131,451 \text{ kJ} \quad (4.52)$$

The charging exergy efficiency is

$$\psi_c = \frac{27,399}{131,451} = 0.21 \quad (4.53)$$

#### 4.4.3.2 Discharging Process

The discharging exergy efficiency can be evaluated using Equation (4.33). For the inlet and outlet conditions of the working fluid (water), the relevant properties are as follows:

- $h_3 = 104.8 \text{ kJ/kg}$  (at  $T_3 = 25 \text{ }^\circ\text{C}$ ,  $P_3 = 101 \text{ kPa}$ )
- $s_3 = 0.3669 \text{ kJ/kg K}$  (at  $T_3 = 25 \text{ }^\circ\text{C}$ ,  $P_3 = 101 \text{ kPa}$ )
- $h_4 = 146.7 \text{ kJ/kg}$  (at  $T_4 = 35 \text{ }^\circ\text{C}$ ,  $P_4 = 101 \text{ kPa}$ )
- $s_4 = 0.5049 \text{ kJ/kg K}$  (at  $T_4 = 35 \text{ }^\circ\text{C}$ ,  $P_4 = 101 \text{ kPa}$ )

During discharging,  $\text{SrBr}_2 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  are reactants and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  is the product. The standard chemical exergy of each of the components, their number of moles and the mass of the working are the same as in the energy efficiency calculations. Consequently, the discharging exergy efficiency is

$$\psi_d = \frac{15,055 \text{ kg} \times (104.8 \text{ kJ/kg} - 146.7 \text{ kJ/kg} - 298 \text{ K} \times (0.3669 \text{ kJ/kg K} - 0.5049 \text{ kJ/kg K}))}{(645 \text{ mol} \times 158.43 \text{ kJ/mol}) - [(645 \text{ mol} \times 154.65 \text{ kJ/mol}) + (3198 \text{ mol} \times 9.33 \text{ kJ/mol})]} = 0.42 \quad (4.54)$$

#### 4.4.4 Energy and Exergy Analyses of Overall TES Process

The energy efficiency of the overall TES process can be written as the ratio of the energy recovered from the TES during discharging to the energy input during charging, as expressed in Equation (4.37). In this equation, the mass flows of the working fluid during charging and discharging have been evaluated before and are equal to 14,866 kg and 15,055 kg, respectively. The enthalpy, entropy, temperature difference and  $C_p$  of the working fluids are known. Thus,

$$\eta_o = \frac{15,055 \text{ kg} \times 4.183 \text{ kJ/kg K} \times (35 - 25) \text{ K}}{14,866 \text{ kg} \times 4.183 \text{ kJ/kg K} \times (70 - 50) \text{ K}} = 0.50 \quad (4.55)$$

Analogously, the exergy efficiency of the overall TES process can be written using Equation (4.41). In this equation, the mass of the working fluid for the charging and the discharging process as well as enthalpy and entropy of the inlet and outlet working fluid have been evaluated previously. Thus,

$$\psi_o = \frac{15055 \text{ kg} \times (104.8 \text{ kJ/kg} - 146.7 \text{ kJ/kg} - 298 \text{ K} \times (0.3669 \text{ kJ/kg K} - 0.5049 \text{ kJ/kg K}))}{14866 \text{ kg} \times (293.1 \text{ kJ/kg} - 209.4 \text{ kJ/kg} - 298 \text{ K} \times (0.9549 \text{ kJ/kg K} - 0.7037 \text{ kJ/kg K}))} = 0.09 \quad (4.56)$$

#### 4.4.5 Summary of Efficiencies for Thermochemical TES Processes

The efficiencies obtained here for the overall TES process considered in the illustrative example and its steps are summarized in Table 4.3.

**Table 4.3. Energy and exergy efficiencies for the TES considered in the illustrative example.\***

Process	Efficiency		
	Type	Expression	Value
Charging	Energy	$\eta_c = \frac{\Delta H_{reaction}}{m_c C_p (T_1 - T_2)}$	0.86
	Exergy	$\psi_c = \frac{\Delta \epsilon_{reaction}}{m_c [h_1 - h_2 - T_0 (s_1 - s_2)]}$	0.21

Discharging	Energy	$\eta_d = \frac{m_d C_p (T_4 - T_3)}{\Delta H_{reaction}}$	0.58
	Exergy	$\psi_d = \frac{m_d [h_4 - h_3 - T_0 (s_4 - s_3)]}{\Delta E_{reaction}}$	0.42
Overall	Energy	$\eta_o = \frac{m_d C_p (T_4 - T_3)}{m_c C_p (T_1 - T_2)}$	0.50
	Exergy	$\psi_o = \frac{m_d [h_4 - h_3 - T_0 (s_4 - s_3)]}{m_c [h_1 - h_2 - T_0 (s_1 - s_2)]}$	0.09

\* The energy and exergy efficiencies of the storing process in this analysis are equal to 1.0, since it is assumed that there are no energy losses during the storing period.

## 4.5 Discussion

The methodology applied in this analysis, based on energy and exergy, is similar to that employed for analyses of other types of TES systems. General efficiency expressions are determined for the charging, storing and discharging processes, as well as the overall TES process. These efficiencies are calculated for an illustrative example based on an actual system. Exergy analysis is seen to be useful, when applied with or in place of energy analysis, for assessing efficiencies of the various processes occurring in TES systems as well as other aspects of their thermodynamic performances. Exergy analysis is more useful than energy analysis for identifying the locations and reasons of thermodynamic losses in a TES system and can assist efforts to improve or optimize designs. Such efforts contribute to society's efforts to achieve more advanced, clean and efficient energy systems.

Efficiencies of the storing process have been taken to be 100%, based on the assumption that there is no energy loss during storing period. This assumption is likely reasonable, in that the materials stored are at ambient conditions so no heat losses are expected. Nonetheless, the storing-period efficiencies could be lower than 100%, depending on the characteristics of the thermochemical material, the working fluid, the storing temperature, the storing duration, etc.

In this study, a single cycle of TES system operation is considered. Therefore, degradation of the thermochemical materials over time, as they undergo repeated cycles, is not considered. However, the effects of degradation are potentially significant, especially if it is found that repeated thermochemical cycles affect performance and the properties of the thermochemical material degrade notably over time. Side reactions cause degradation of thermochemical materials over number of cycles which lead thermochemical materials not to reverse back to their initial state. Therefore, the heat recovered by the storage system may reduce over time.

A TES system for heating capacity only is investigated here. The system considered in the illustrative example supplies heat to the floor of a building during winter or mid-season periods. With an analogous approach, it is possible that cold TES systems could be assessed in terms of efficiency, cost, thermochemical materials and other factors.

For the illustrative example, the energy and exergy efficiencies respectively are determined to be 86% and 21% for the charging process and 58% and 42% for the discharging process. The results demonstrate that the energy efficiency of the charging process is higher than the corresponding efficiency for the discharging process and that the exergy efficiency of the discharging process is higher than the corresponding efficiency for the charging process. The overall energy and exergy efficiencies are found to be 50% and 9%, respectively. The results demonstrate that the energy efficiencies of the charging and overall processes are higher than the corresponding exergy efficiencies. Exergy analysis takes into account the loss of availability of energy in a thermochemical TES system and indicates the thermodynamic and economic value of the system. The differences between energy and exergy efficiencies for the thermochemical TES and its processes are dependent

on various factors, including the characteristics of the working fluid and thermochemical material, the nature of the synthesis or dissociation reaction, the desired heating temperature, the maximum output temperature of the heat source (a flat solar collector in the case study), and the level of insulation on the TES and associated piping. The TES energy or exergy losses likely vary with all of these factors and others.

The factors discussed above suggest that the performance attained with other types of TES (sensible and latent) may be attained with thermochemical TES, but with more compact storage systems.

# Chapter 5

## Energy and Exergy Analysis of an Open Thermochemical Energy Storage System

### 5.1 Introduction

Thermochemical TES systems can be classified as closed or open (Bales, 2005). In closed systems, internal substances are separate from the heat transport fluid while in open systems, internal substances are not separate from the heat transport fluid.

Closed systems can provide higher output temperature than open systems in heating applications (Hauer, 2008). Charging processes in closed systems usually need higher temperatures than open systems (Hauer and Lavemann, 2007).

In open thermochemical energy storage, the basic operating principle is the same as for closed thermochemical TES. The main chemical reaction can be expressed as follows:



In open thermochemical TES, the heat transport fluid is not separate from materials A, B and C. Open thermochemical TES systems operate in an open loop coupled to the ambient conditions and an air stream transports water vapor and heat in and out of the packed bed of thermochemical materials (Hauer, 2007). Open sorption storage is a type of open thermochemical TES. Open sorption systems operate at the atmospheric pressure and the working fluid vapor is released to the environment (Edem et al., 2009; Hauer, 2007). Two examples of applications of open sorption TES in energy systems follow. Sorption systems in the Monosorp project have been

examined by the Institute of Thermodynamics and Thermal Engineering at the University of Stuttgart (Bales, 2006). Sorption energy storage as part of a district heating grid in Munich (Hauer, 2002) has been studied by the Bavarian Center for Applied Energy Research (ZAE Bayern).

In this chapter, a detailed investigation based on energy and exergy is carried out of an open thermochemical TES. An illustrative example is included based on experimental data from the open literature.

## **5.2 Energy and Exergy Analyses**

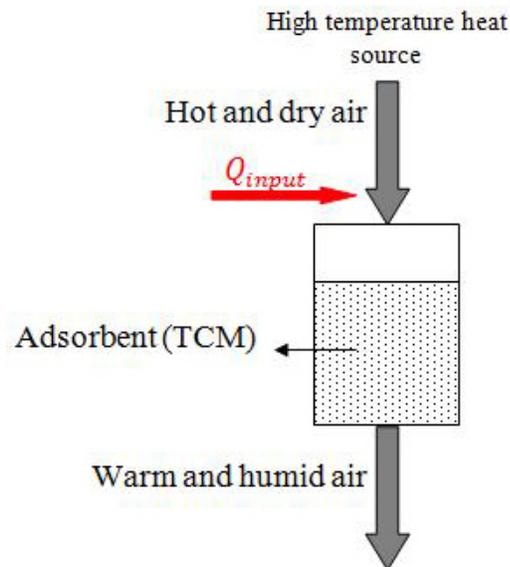
A general open thermochemical TES is considered and energy and exergy analyses are performed. The system considered, consists of a working fluid (air) and a thermochemical material. Thermal energy from an energy supply (e.g. a district heating system) is transferred to air and provides the energy necessary for desorption of the thermochemical material. After a storing period, energy released from adsorption of the thermochemical material warms air to be used for heating purposes.

This analysis is limited to open TES systems where internal substances are not separate from the heat transport fluid. The following assumptions are made in this investigation:

- Chemical reactions within the reactor occur at constant pressure.
- Work interactions into and out of the control volume are neglected, as are kinetic and potential energy. The former assumption implies that pump, compressor and fan work are neglected.
- The physical exergy change of the components is neglected relative to their chemical exergy changes.

### 5.2.1 Charging (Desorption) Process

A general charging process for an open thermochemical TES is illustrated in Figure 5.1. A hot air stream, heated by a high temperature heat source, flows through the storage, desorbs the water from the adsorbent (thermochemical material) and dries it, and exits the packed bed a lower temperature and a higher humidity. The process is endothermic and the net energy input to the packed bed  $Q_{input}$  is supplied by the input air.



**Figure 5.1. Desorption (charging) process in open thermochemical TES. Adapted from Hauer (2002).**

#### 5.2.1.1 Energy Analysis for Charging

A general energy balance for the charging process of a TES can be written as (Dincer and Rosen, 2002):

$$\text{Energy input} - \text{Energy output} = \text{Energy accumulation} \quad (5.2)$$

The net input energy is supplied by the air flow for this system. Analogously with the closed loop system, an energy balance for the charging process can be written as follows:

$$\text{Net energy input} - \text{Heat loss} = \text{Energy accumulation in TES} \quad (5.3)$$

or

$$Q_{input} - Q_{loss} = \Delta H_{ds} \quad (5.4)$$

where  $Q_{input}$  is the net energy input to the system during the charging process and  $Q_{loss}$  denotes the total heat loss. The term  $\Delta H_{ds}$  is the enthalpy change of the desorption process.

The energy efficiency of the charging process can be expressed as follows:

$$\eta_c = \frac{\text{Energy gained by adsorbent}}{\text{Energy input}} = \frac{\Delta H_{ds}}{Q_{input}} \quad (5.5)$$

### 5.2.1.2 Exergy Analysis for Charging

A general exergy balance for this system can be written as

$$\text{Exergy input} - \text{Exergy loss} - \text{Exergy destruction} = \text{Exergy accumulation} \quad (5.6)$$

or

$$\epsilon_{input} - \epsilon_{loss} - \epsilon_D = \Delta \epsilon_{ds} \quad (5.7)$$

Here,

$$\epsilon_{input} = \text{Exergy input} = \text{Net exergy delivered by air} \quad (5.8)$$

Also,  $\epsilon_D$  denotes the exergy destruction,  $\epsilon_{loss}$  the exergy loss, and  $\Delta \epsilon_{ds}$  the exergy accumulation in the charging process, which can be evaluated with the same method used for closed TES systems.

We can evaluate the exergy efficiency of the charging process as follows:

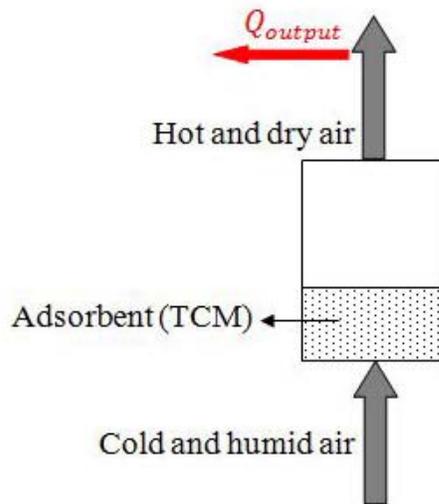
$$\psi_c = \frac{\text{Exergy stored in desorption}}{\text{Exergy input}} = \frac{\Delta\epsilon_{ds}}{\epsilon_{input}} \quad (5.9)$$

### 5.2.2 Storing Process

Using similar assumptions as applied in the analysis of closed thermochemical TES, the energy and exergy efficiencies of the storing process are equal to unity.

### 5.2.3 Discharging (Adsorption) Process

A general discharging process for an open thermochemical TES is illustrated in Figure 5.2. The previously humidified, cool indoor air enters the desorbed packed bed. Then, the adsorbent adsorbs water vapor from the air flow and releases the heat of adsorption ( $Q_{output}$ ). The process is exothermic.



**Figure 5.2. Adsorption (discharging) process in open thermochemical TES. Adapted from Hauer (2002).**

### 5.2.3.1 Energy Analysis for Discharging

We can write an energy balance for the discharging period for a TES as follows (Dincer and Rosen, 2002):

$$-[Energy\ recovered + Heat\ Loss] = Energy\ accumulation \quad (5.10)$$

The recovered energy is gained by the air flow for this process. We can evaluate the energy efficiency of this process as follows:

$$\eta_d = \frac{Energy\ recovered}{Energy\ released\ in\ adsorption} = \frac{Q_{recovered}}{\Delta H_{ad}} \quad (5.11)$$

### 5.2.3.2 Exergy Analysis for Discharging

We can write an exergy balance for the discharging process as follows:

$$-(Exergy\ recovered + Exergy\ loss) - Exergy\ destruction = Exergy\ accumulation \quad (5.12)$$

or

$$-(\epsilon_{recovered} + \epsilon_{loss}) - \epsilon_D = \Delta \epsilon_{ad} \quad (5.13)$$

Here,

$$\epsilon_{recovered} = Exergy\ recovered = Net\ exergy\ recovered\ by\ air \quad (5.14)$$

where  $\Delta \epsilon_{ad}$  denotes the exergy accumulation in the discharging process. We can evaluate the exergy efficiency of this process as

$$\psi_d = \frac{Exergy\ recovered\ by\ air}{Exergy\ released\ in\ adsorption} = \frac{\epsilon_{recovered}}{\Delta \epsilon_{ad}} \quad (5.15)$$

## 5.2.4 Overall Process

The energy and exergy analyses of the overall processes are considered in this section.

### 5.2.4.1 Energy Balance and Efficiency for Overall Process

An energy balance for the overall open thermochemical storage process can be written as

$$\text{Energy input} - \text{Energy recovered} - Q_{loss,tot} = \Delta E \quad (5.16)$$

For the case of a complete cycle with identical initial and final states,  $\Delta E = 0$ .

The energy efficiency for the overall storage process can be written as follows:

$$\eta_o = \frac{\text{Energy recovered from TES during adsorption}}{\text{Energy input to TES during desorption}} = \frac{Q_{recovered}}{Q_{input}} \quad (5.17)$$

### 5.2.4.2 Exergy Balance and Efficiency for Overall Process

An exergy balance for the overall storage process can be written as

$$\text{Exergy input} - \text{Exergy recovered} - \epsilon_{loss,tot} - \epsilon_{D,tot} = \Delta \epsilon \quad (5.18)$$

For the case of a complete cycle with identical initial and final states,  $\Delta \epsilon = 0$ .

The exergy efficiency for the overall storage process can be expressed as follows:

$$\psi_o = \frac{\text{Exergy recovered from TES during adsorption}}{\text{Exergy input to TES during desorption}} = \frac{\epsilon_{recovered}}{\epsilon_{input}} \quad (5.19)$$

## 5.3 Illustrative Example

To illustrate the analysis of an open thermochemical TES system, we consider an existing system for which experimental data have been reported.

### 5.3.1 System Description

An open sorption system has been utilized in a school in Munich, Germany since 1996. This system is connected to the district heating net. This thermochemical storage uses zeolite 13X as the adsorbent and can provide heating in winter as well as

an air conditioning possibility in summer. This system is used to heat a school building in winter and cool a jazz club in summer. Both the school building and jazz club are connected to the Munich district heating system. The storage system is connected to a combined air, radiator and floor heating system (Hauer, 2002).

The storage contains 7,000 kg of zeolite 13X beads. Zeolite 13X is non-toxic and non-flammable and can be handled easily. The maximum air flow through the zeolite storage is 6,000 m<sup>3</sup>/h (Hauer, 2007). The heating mode of the system (applicable during winter) is investigated in this study. An energy storage density of 135 kWh/m<sup>3</sup> (0.5 GJ/m<sup>3</sup>) can be obtained in the heating mode of the storage (Fischer and Hauer, 1998).

The following assumptions are made in this investigation:

- The maximum storage capacity is utilizable in the charging process.
- The formula for zeolite 13X is Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·3SiO<sub>2</sub>·6H<sub>2</sub>O.
- Zeolite 13X has a maximum water uptake during the charging process and dried zeolite 13X hydrates have the maximum number of water molecules.
- The maximum volumetric air flow rate (6,000 m<sup>3</sup>/h) occurs during charging and discharging.
- The energy changes during adsorption and desorption are equal in magnitude, i.e.  $\Delta H_{ad} = -\Delta H_{ds}$ .
- The exergy changes during adsorption and desorption are equal in magnitude, i.e.  $\Delta \epsilon_{ad} = -\Delta \epsilon_{ds}$ .

The effect of the assumptions made in this study can be investigated on the efficiency results. It is particularly important to note that in this investigation the maximum storage capacity is considered and the volumetric air flow rate during charging and discharging processes is assumed to have its maximum value. With

additional practical data, these values may vary and efficiencies and other results will change correspondingly.

### 5.3.2 Charging Process

The thermochemical storage is charged when energy is available from the district heating system in off-peak hours. Charging is performed during 10 hours nightly (from 9 p.m. to 7 a.m.) each day.

The charging process is illustrated in Figure 5.3. At first the air is heated from 25 °C to 130 °C by the district heating system. At night, the zeolite is charged using the air. Under these conditions zeolite is dried and the waste heat of the charging process at a temperature level of 35-40 °C supplies the heating system of the school. The maximum storage capacity of the charging process is 1,400 kWh at a charging temperature of 130 °C (Hauer, 2002). As noted earlier, it is assumed that the maximum storage capacity can be obtained during charging. Temperatures and the maximum storage capacity are optimistic according to the design conditions.

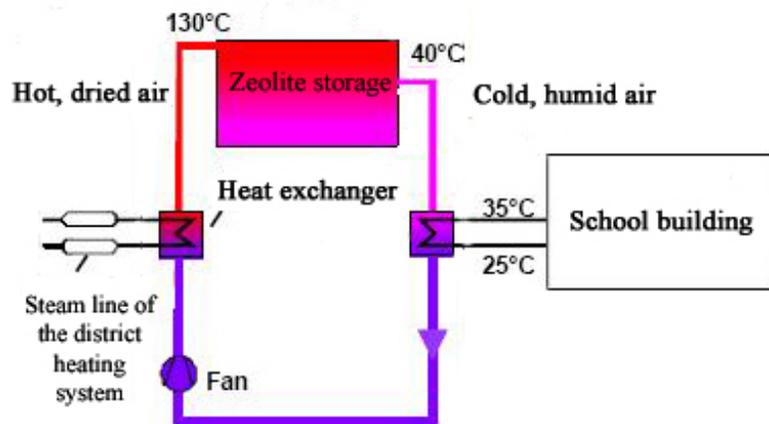
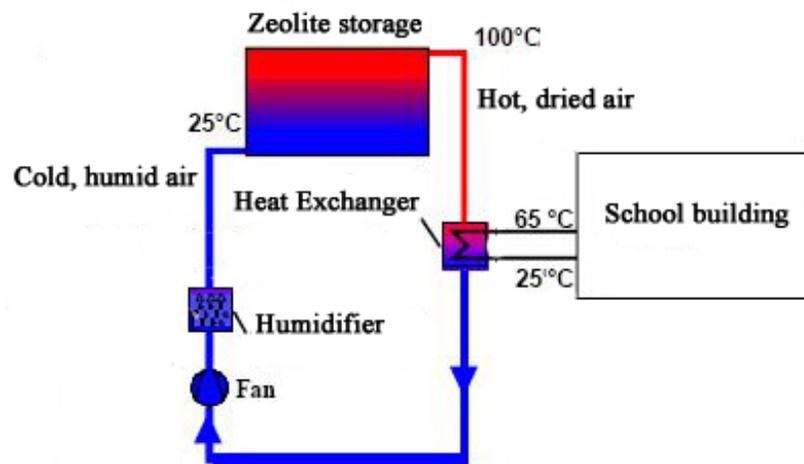


Figure 5.3. Charging (desorption) process at night. Adapted from Hauer (2002).

### 5.3.3 Discharging Process

The thermochemical storage is discharged during daytime (the peak period). The discharging process is illustrated in Figure 5.4. Air is heated to 25 °C and saturated with water vapor by a humidifier. Then, the saturated air is blown through the storage of dried zeolite. The air temperature rises to 100 °C.

Discharging occurs over 14 hours (from 7 a.m. to 9 p.m.) each day and can provide a maximum heating power of 95 kW at an outdoor temperature of -16 °C (Hauer, 2002).



**Figure 5.4. Discharging (adsorption) process during the day. Adapted from Hauer (2002).**

### 5.3.4 Energy Analysis of TES Processes

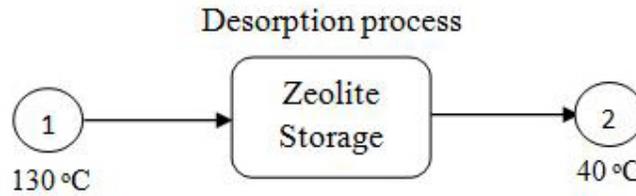
Energy efficiencies are determined for the charging and discharging processes for the considered thermochemical TES, as well as for the overall process. Note that the energy efficiency for the storing period is not discussed extensively, as it is 100%.

### 5.3.4.1 Charging

The charging energy efficiency can be calculated using Equation (5.5). We calculate the energy efficiency of each process as the ratio of the useful energy output to the energy input as follows:

$$\eta_c = \frac{\text{useful output energy}}{\text{input energy}} \quad (5.20)$$

In this analysis, the zeolite storage is taken to be the control volume (see Figure 5.5). In the charging process, the useful output energy is equal to the storage capacity of the charging process, which is 1,400 kWh (or 5,040,000 kJ).



**Figure 5.5. Desorption process with inlet and outlet conditions of the air stream.**

The input energy is supplied by the air flow and can be calculated as

$$Q_{input} = m_c C_p (T_1 - T_2) \quad (5.21)$$

Here,  $m_c$  is the mass of air which blows through the storage during the charging period and can be calculated as

$$m_c = q_c t_c \rho_c \quad (5.22)$$

where  $q_c$  denotes the volumetric air flow rate, and  $t_c$  and  $\rho_c$  are charging time and air density, respectively. The density and specific heat at constant pressure  $C_p$  of the air are evaluated at the mean temperature of the inlet and outlet air (77.5 °C). Thus,

$$m_c = 6,000 \text{ m}^3/\text{h} \times 10 \text{ h} \times 1.004 \text{ kg}/\text{m}^3 = 60,240 \text{ kg} \quad (5.23)$$

So, the input energy is

$$Q_{input} = 60,240 \times 1.008 \times (130 - 40) = 5,464,972 \text{ kJ} \quad (5.24)$$

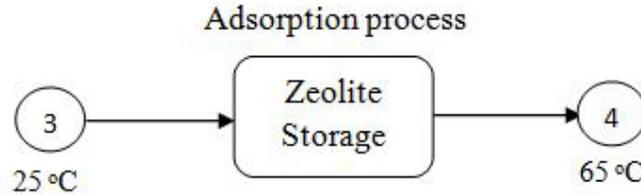
The useful output energy is 5,040,000 kJ and the charging energy efficiency is:

$$\eta_c = \frac{\text{useful output energy}}{\text{input energy}} = \frac{5,040,000}{5,464,972} = 0.92 \quad (5.25)$$

Comparing Equations (5.5) and (5.20), it is observed that the energy gained in the desorption process is equal to the numerator of the efficiency equation (5,040,000 kJ). Since the reaction is reversible, the energy released during the adsorption process is 5,040,000 kJ as well.

### 5.3.4.2 Discharging

The discharging energy efficiency is calculated using Equation (5.11). In this analysis, the zeolite storage is taken to be the control volume (see Figure 5.6).



**Figure 5.6. Adsorption process with inlet and outlet conditions of the air stream.**

The recovered energy can be calculated as

$$Q_{recovered} = m_d C_p (T_4 - T_3) \quad (5.26)$$

The quantity  $m_d$  is the mass of air which passes through the storage during the discharging period and can be calculated as

$$m_d = q_d t_d \rho_d \quad (5.27)$$

Here,  $q_d$  denotes the volumetric air flow rate.  $t_d$  and  $\rho_d$  are discharging time and density of air, respectively.

The density and  $C_p$  of the air are evaluated at the mean temperature of the inlet and outlet air (45 °C), thus

$$m_d = 6,000 \text{ m}^3/\text{h} \times 14 \text{ h} \times 1.106 \text{ kg}/\text{m}^3 = 92,904 \text{ kg} \quad (5.28)$$

Thus

$$Q_{recovered} = m_d C_p (65 - 25) = 92,904 \times 1.106 \times 40 = 4,110,073 \text{ kJ} \quad (5.29)$$

The discharging energy efficiency is

$$\eta_d = \frac{4,110,073}{5,040,000} = 0.81 \quad (5.30)$$

### 5.3.4.3 Overall TES Process

The energy efficiency of the overall TES process can be calculated using Equation (5.17):

$$\eta_o = \frac{Q_{recovered}}{Q_{input}} = \frac{4,110,073}{5,464,972} = 0.75 \quad (5.31)$$

### 5.3.5 Exergy Analysis of TES Processes

Charging, discharging and overall exergy efficiencies are determined for the considered thermochemical TES. As before, the exergy efficiency for the storing period (100%) is not discussed extensively.

#### 5.3.5.1 Charging

The exergy efficiency of the charging process can be evaluated using Equation (5.9). During charging, air is heated from 40 °C to 130 °C. The exergy input for the charging process can be evaluated as

$$\text{Exergy input} = \text{Net exergy delivered by air} = m_c[h_2 - h_1 - T_0(s_2 - s_1)] \quad (5.32)$$

where  $h_1$  and  $h_2$  denote the specific enthalpy of the air at the input and output conditions,  $s_1$  and  $s_2$  denote the specific entropy of the air at the input and output conditions. The relevant properties of the air are as follows:

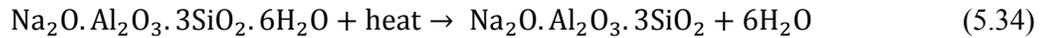
- $h_1 = 313.16 \text{ kJ/kg}$  (at  $T_1 = 40 \text{ }^\circ\text{C}$ ,  $P_1 = 101 \text{ kPa}$ )
- $s_1 = 5.746 \text{ kJ/kg K}$  (at  $T_1 = 40 \text{ }^\circ\text{C}$ ,  $P_1 = 101 \text{ kPa}$ )
- $h_2 = 404.5 \text{ kJ/kg}$  (at  $T_2 = 130 \text{ }^\circ\text{C}$ ,  $P_2 = 101 \text{ kPa}$ )
- $s_2 = 6 \text{ kJ/kg K}$  (at  $T_2 = 130 \text{ }^\circ\text{C}$ ,  $P_2 = 101 \text{ kPa}$ )

The exergy input in the charging process can be calculated using Equation (5.32):

$$\epsilon_{input} = 60,240 \times [404.5 - 313.16 - 298 \times (6 - 5.746)] = 942,635 \text{ kJ} \quad (5.33)$$

The exergy stored during the charging process can be calculated following the same methodology used for the closed thermochemical TES.

A typical chemical formula for zeolite 13X composition is  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (2.8 \mp 0.2)\text{SiO}_2 \cdot (6\sim 7)\text{H}_2\text{O}$ . We assume the formula for zeolite 13X in this study as  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ . The molecular weight for zeolite 13X is 452.3 grams. There are 7,000 kg of zeolite in the storage system, so the numbers of moles of zeolite 13X is 15,476. The charging reaction can be expressed as



In order to calculate the exergy stored in this reaction, we need to evaluate the standard chemical exergy of each component (see Table 5.1). The standard chemical exergy of a chemical compound  $\epsilon_{chn}$  can be calculated by means of the exergy balance for a reversible reaction:

$$\epsilon_{chn} = \Delta G_f + \sum_e n_e \epsilon_{chne} \quad (5.35)$$

Here,  $\Delta G_f$  denotes the Gibbs energy of formation,  $n_e$  the amount of element  $e$  (in kmol), and  $\epsilon_{chne}$  the standard chemical exergy of the element.

**Table 5.1. Evaluating standard chemical exergy of selected components for normal reference-environment conditions ( $T_0 = 298.15$  K;  $P_0 = 101.325$  kPa).**

Compound	$\Delta G_f$ (kJ/mol)	$n_e$		$\epsilon_{chne}$ (kJ/mol)		$\epsilon_{chn}$ (kJ/mol)
				(Na)	(O <sub>2</sub> )	
Na <sub>2</sub> O	-262.05	2 (Na)	0.5 (O <sub>2</sub> )	336.6 (Na)	3.97 (O <sub>2</sub> )	413.14
Al <sub>2</sub> O <sub>3</sub>	-1582.19	2 (Al)	1.5 (O <sub>2</sub> )	988.2 (Al)	3.97 (O <sub>2</sub> )	400.17
SiO <sub>2</sub>	-851.18	1 (Si)	1 (O <sub>2</sub> )	854.9 (Si)	3.97 (O <sub>2</sub> )	7.69
H <sub>2</sub> O (gas)	-228.75	1 (H <sub>2</sub> )	0.5 (O <sub>2</sub> )	236.09 (H <sub>2</sub> )	3.97 (O <sub>2</sub> )	9.32
H <sub>2</sub> O (liquid)	-237.32	1 (H <sub>2</sub> )	0.5 (O <sub>2</sub> )	236.09 (H <sub>2</sub> )	3.97 (O <sub>2</sub> )	0.76

\* Taken from Woods and Garrels (1987).

Using calculated data from Table 5.1, the standard chemical exergy of zeolite 13X (before and after desorption) can be calculated as follows.  
For Na<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>. 3SiO<sub>2</sub>. 6H<sub>2</sub>O:

$$\epsilon_{chn} = 413.14 + 400.17 + (3 \times 7.69) + (6 \times 0.76) = 840.94 \text{ kJ/mol} \quad (5.36)$$

For Na<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>. 3SiO<sub>2</sub>:

$$\epsilon_{chn} = 413.14 + 400.17 + (3 \times 7.69) = 836.38 \text{ kJ/mol} \quad (5.37)$$

The exergy accumulation during the charging period can be expressed as

$$\text{Exergy stored in desorption} = \epsilon_{tot,products} - \epsilon_{tot,reactants} \quad (5.38)$$

Here, Na<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>. 3SiO<sub>2</sub> and H<sub>2</sub>O are products and Na<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>. 3SiO<sub>2</sub>. 6H<sub>2</sub>O is the reactant, and the corresponding standard chemical exergies of the products and the reactant have been calculated:

$$\begin{aligned} \text{Exergy stored in desorption} &= 15,476 \text{ moles} \times \{[836.38 \text{ kJ/mol} + (6 \times \\ &9.32) \text{ kJ/mol}] - 840.94 \text{ kJ/mol}\} = 794,847 \text{ kJ} \end{aligned} \quad (5.39)$$

Thus, the exergy efficiency of the charging process can be calculated as

$$\psi_c = \frac{\text{Exergy stored in desorption}}{\text{Exergy input}} = \frac{794,847}{942,635} = 0.84 \quad (5.40)$$

### 5.3.5.2 Discharging

The exergy efficiency of the discharging process can be evaluated using Equation (5.15). During discharging, air is heated from 25 °C to 65 °C. The exergy recovered in this process can be evaluated as

$$\text{Net exergy recovered by air} = m_d [h_4 - h_3 - T_0 (s_4 - s_3)] \quad (5.41)$$

where  $h_3$  and  $h_4$  denote respectively the specific enthalpy of the air at the input and output conditions, and  $s_3$  and  $s_4$  respectively denote the specific entropy of the air at the input and output conditions.

Thus, the relevant properties of the air are as follows:

- $h_3 = 298.6 \text{ kJ/kg}$  (at  $T_1 = 25 \text{ °C}$ ,  $P_1 = 101 \text{ kPa}$ )
- $s_3 = 5.696 \text{ kJ/kg K}$  (at  $T_1 = 25 \text{ °C}$ ,  $P_1 = 101 \text{ kPa}$ )
- $h_4 = 338.8 \text{ kJ/kg}$  (at  $T_2 = 65 \text{ °C}$ ,  $P_2 = 101 \text{ kPa}$ )
- $s_4 = 5.823 \text{ kJ/kg K}$  (at  $T_2 = 65 \text{ °C}$ ,  $P_2 = 101 \text{ kPa}$ )

From Equation (5.41):

$$\epsilon_{\text{recovered}} = 92,904 \times [338.8 - 298.6 - 298 \times (5.823 - 5.696)] = 218,696 \text{ kJ} \quad (5.42)$$

So,

$$\psi_d = \frac{\text{Exergy recovered by air}}{\text{Exergy released in adsorption}} = \frac{218,696}{794,847} = 0.28 \quad (5.43)$$

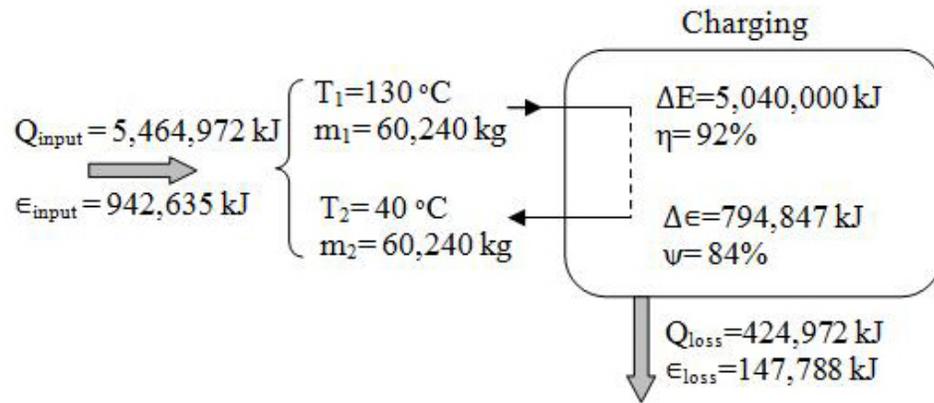
### 5.3.5.3 Overall TES Process

The exergy efficiency of the overall TES process can be calculated using Equation (5.19):

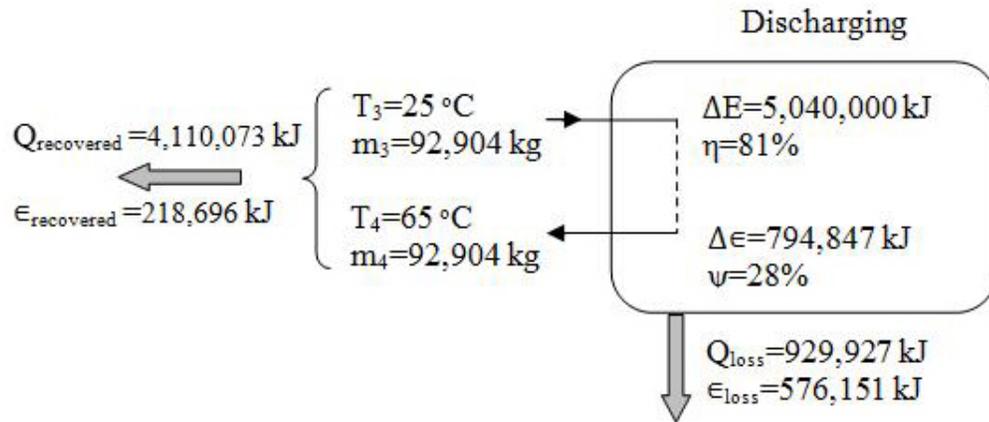
$$\psi_o = \frac{\epsilon_{recovered}}{\epsilon_{input}} = \frac{218,696}{942,635} = 0.23 \quad (5.44)$$

## 5.4 Summary

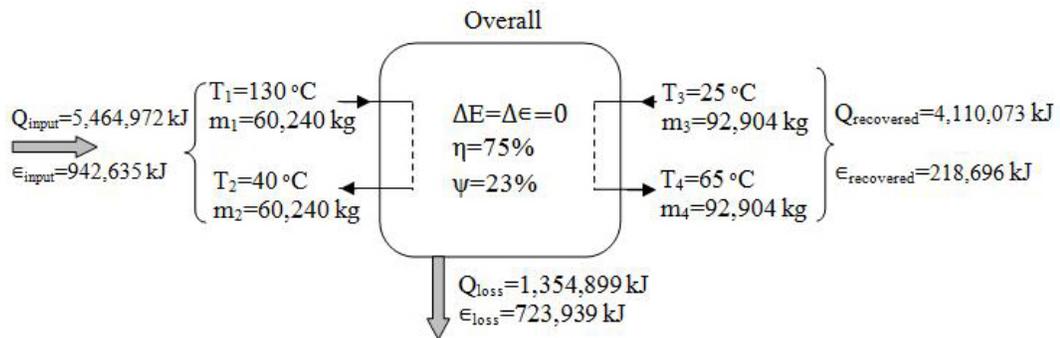
The energy and exergy analyses for the charging and discharging processes are summarized illustratively in Figures (5.7), (5.8) and (5.9). Note that  $\epsilon_{loss}$  in these diagrams is the summation of the exergy loss and the exergy destruction.



**Figure 5.7. The charging process, showing energy and exergy parameter values.**



**Figure 5.8. The discharging process, showing energy and exergy parameter values.**



**Figure 5.9. The overall storage process, showing energy and exergy parameter values.**

## 5.5 Discussion

The energy- and exergy-based methodology applied here is similar to that employed for analyses of other types of TES systems. General efficiency expressions are determined for the charging, storing and discharging processes, as well as the overall TES process. These efficiencies are calculated for an illustrative example, based on an actual system.

Exergy analysis is seen to be useful, when applied with or in place of energy analysis, for assessing efficiencies of the various processes occurring in open

thermochemical TES systems as well as other aspects of their thermodynamic performances. Exergy analysis is more useful than energy analysis for identifying the locations and reasons of thermodynamic losses in a TES system and can assist efforts to improve or optimize designs. The energy loss of the overall process is 1,354,799 kJ and the exergy loss of the overall storage system is 723,939 kJ. It is seen in Figures (5.7-9) that 69% of the total energy loss and 79% of the total exergy loss occur during discharging. So, optimizing the discharging process can help to improve the overall efficiency of the storage process.

Efficiencies of the storing process have been taken to be 100%, based on the assumption that there is no energy loss during storing period. This assumption is likely reasonable, in that the materials stored are at ambient conditions so no heat losses are expected. Nonetheless, the storing-period efficiencies could be lower than 100%, depending on the characteristics of the thermochemical material, the working fluid, the storing temperature, the storing duration, etc.

In this study, a single cycle of an open TES system operation is considered. Therefore, degradation of the thermochemical materials over time, as they undergo repeated cycles, is not considered. However, the effects of degradation are potentially significant, especially if repeated thermochemical cycles affect performance and the properties of the thermochemical material degrade notably over time. Little information on the degradation of thermochemical storage materials is available, but it is noted that phase change materials (PCMs) are also degraded with cycling in latent TES systems. Sari and Karaipekli (2009) investigated the characterization and thermal properties of palmitic acid/expanded graphite as a PCM in latent TES systems and showed that, after 3,000 melting/freezing cycles, the melting latent heat decreased

from 148.36 kJ/kg to 140.38 kJ/kg and freezing latent heat decreased from 149.66 kJ/kg to 139.97 kJ/kg.

A TES system for heating capacity only is investigated here. The system considered in the illustrative example supplies heat to a school building during winter or mid-season periods. The storage of cooling capacity is not considered.

For the illustrative example, the energy and exergy efficiencies respectively are determined to be 92% and 84% for the charging process and 81% and 28% for the discharging process. The results demonstrate that the energy efficiency of the discharging process is higher than the corresponding efficiency for the charging process and that the exergy efficiency of the charging process is higher than the corresponding efficiency for the discharging process. The overall energy and exergy efficiencies are found to be 75% and 23%, respectively. The results demonstrate that the exergy efficiencies of the charging, discharging, and overall processes are higher than the corresponding energy efficiencies. Exergy analysis takes into account the loss of availability of energy in storage operations and it reflects the thermodynamic and economic value of the storage operation. In the analyses, the maximum flow rate has been considered for the air and also it has been assumed that zeolite 13X is dried during desorption process to the maximum extent possible. Therefore, the energy gained by the adsorbent attains a maximum value. The same assumption has been made for the adsorption process.

Exergy analysis takes into account the loss of availability of energy in a thermochemical TES system and indicates the thermodynamic and economic value of the system. The differences between energy and exergy efficiencies for the thermochemical TES and its processes are dependent on various factors, including the thermodynamic properties of the working fluid (air) and the thermochemical material,

the nature of the desorption or adsorption process, the maximum output temperature of the heat source (a district heating system in the case study). The TES energy or exergy losses likely vary with all of these factors and others.

The factors discussed above suggest that the performance attained with other types of TES (sensible and latent) may be attained with open thermochemical TES, but with more compact storage systems. Efficiencies of various types of TES systems are compared Table 5.2.

**Table 5.2. Comparison of efficiencies for various types of TES.**

<b>TES type</b>		<b><math>\eta_o</math></b>	<b><math>\psi_o</math></b>	<b>Remarks</b>
Sensible		70%	40%	Aquifer TES (Rosen, 1999)
Latent		45%	2.2%	CaCl <sub>2</sub> .6H <sub>2</sub> O as PCM (Koca et al., 2008).
Thermochemical	Closed-loop	50%	9%	SrBr <sub>2</sub> .6H <sub>2</sub> O as TCM (Mauran et al., 2008)
	Open-loop	75%	23%	Zeolite 13X as TCM (Hauer, 2002)

# Chapter 6

## Designing Thermochemical TES Systems

### 6.1 Introduction

The design of thermochemical energy storage systems is complex and requires appropriate consideration of many factors. Thermochemical TES systems experience thermochemical interactions with their surroundings, including heat transfer after and before a chemical process. Many criteria need to be considered by engineers in engineering design in designing thermochemical TES systems such as cost, environmental impact, safety, reliability, efficiency, size, and maintenance. Usually, difficulties and complexities exist in design processes and need to be analyzed carefully.

The design of thermochemical energy storage systems is investigated in this chapter. Some important factors related to design concepts of thermochemical TES systems are considered and preliminary design conditions for them are investigated.

### 6.2 Key Factors in the Design of a Thermochemical Storage System

Systems design for thermochemical energy storage, like for general thermal systems, requires that two main categories be considered (Bejan et al., 1996; Stoecker, 1980). Each category is investigated in this study.

- **Component design:** This task refers to the components (hardware parts) of the system, e.g. reactor, heat exchanger, pumps, fans, etc.

- **System design:** This task refers to the overall thermochemical system design, e.g. open or closed loop concept, maintenance, reliability, degradation of thermochemical material, safety, environmental aspects, efficiency, cost, size, etc.

## 6.2.1 Component Design

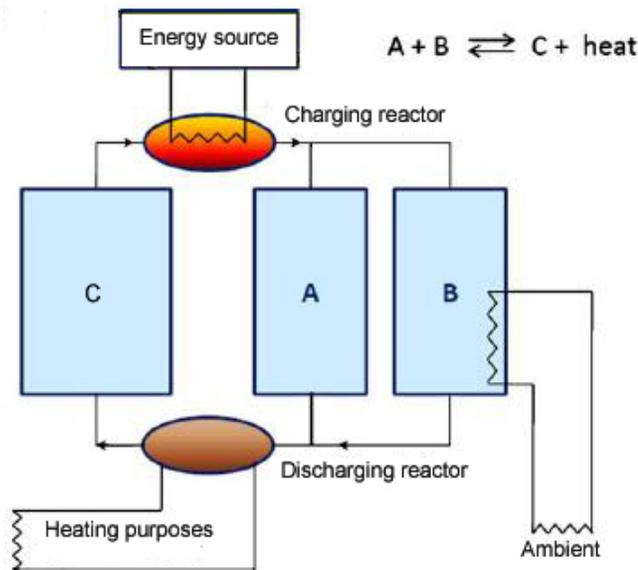
A reactor design for the thermochemical process is selected in this section, and some important related factors are investigated.

### 6.2.1.1 Reactor

The chemical reaction in a thermochemical process takes place in a reactor. There are two types of design concepts for reactors in thermochemical TES systems:

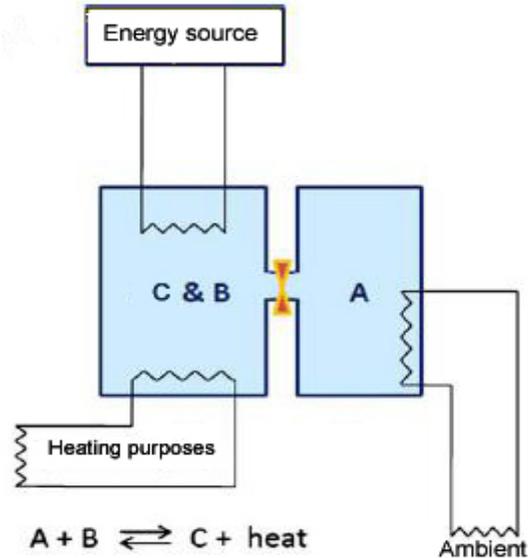
- **Separate reactors:** This type of reactor design is illustrated in Figure 6.1. Thermochemical material C absorbs energy from an energy resource and is converted to components A and B, which are separately stored. In cases in which component B is in a gaseous phase, the ambient air can be used as to condense B so it can be stored as a liquid at a lower temperature. The storing process is simpler in the liquid phase. In addition, the heat of condensation can be used for heating purposes. Separate reactors are suitable for long-term storage, e.g. seasonal storage when large storage capacity is required. The charging process is more efficient in this type of reactor because a specific amount of thermochemical material can be heated from the ambient temperature at the beginning of charging process (preheating) according to the desired power. On the other hand, the heat exchanger surface is smaller than

with integrated reactors and consequently insulating the reactor is easier with separate rather than integrated reactors.



**Figure 6.1. Separate reactors in thermochemical TES systems. Adapted from Edem et al. (2009) and Zondag et al. (2008).**

- **Integrated reactors:** This type of reactor is integrated in the storage and is illustrated in Figure 6.2. Since component B is a solid after the charging process, it can be stored in the same reactor as the thermochemical material C, avoiding the need for a space to store it. Integrated reactors are normally used when the thermochemical material is a solid because it is not necessary to transport solid materials in such reactors. As mentioned earlier, this type of reactor is not suitable for long-term storage because all the thermochemical materials should be heated before charging and, consequently, the efficiency of the charging process is less than for separate reactors (because of the large sensible heat loss). However, the required heat exchange area is larger than for separate reactors and insulating the reactors is more difficult (Edem et al., 2009).



**Figure 6.2. Integrated reactors in thermochemical TES systems. Adapted from Edem et al.(2009) and Zondag et al.(2008).**

### 6.2.1.2 Other Components

The main objective of thermochemical TES systems is to supply a part of heating or cooling loads of an indoor environment. Heat exchangers are normally required in such systems. Selecting efficient heat exchangers is a key requirement for achieving suitable performance of the system and can affect the overall efficiency of the thermochemical application (Edem et al., 2009).

Another key design factor to be considered is insulation. Well-insulated equipment reduces sensible heat losses during each TES process, especially when long-term, e.g. seasonal, storage is used. Reactors, pipelines and heat exchangers are the main components that may incur heat losses. Therefore, they require more attention in terms of appropriate level of insulation.

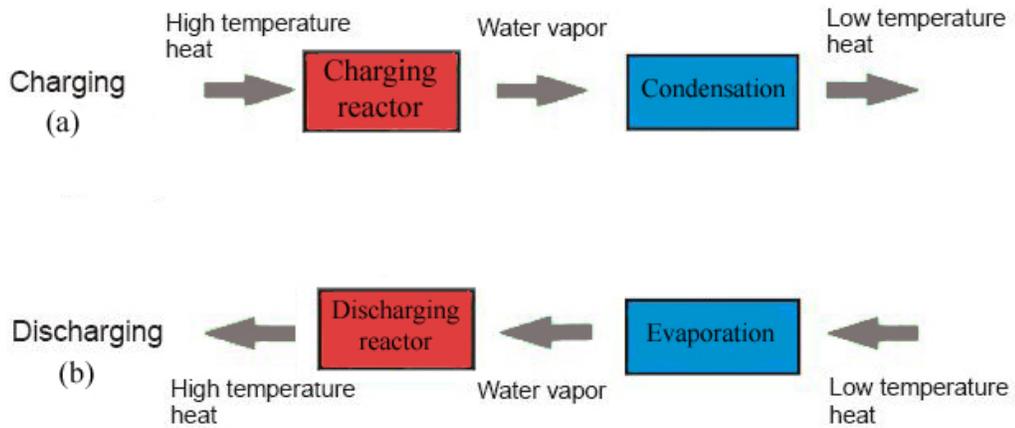
## **6.2.2 System Design**

In this section, closed and open loop concepts, thermochemical materials and their cyclic behaviors, costs, environmental issues and other parameters are considered as they related to the design process of a thermochemical energy storage system.

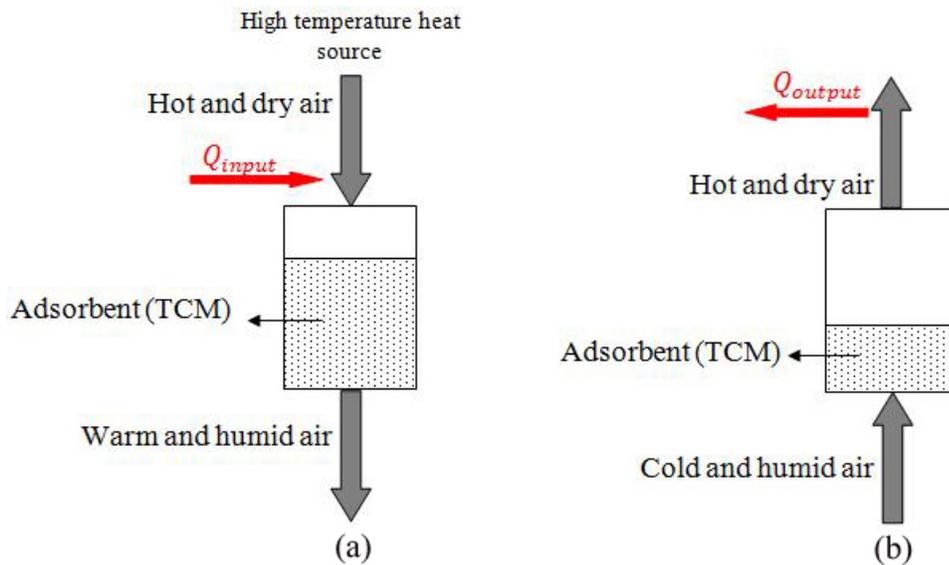
### **6.2.2.1 Closed and Open Loop Thermochemical Energy Storage**

Closed loop and open loop thermochemical systems have been investigated. Briefly, open systems operate at the atmospheric pressure and water vapor is the working fluid, which is released to the ambient environment. In an open system the gaseous working fluid is directly released to the environment and therefore normally only water is a possible candidate as the working fluid. Materials in open systems must be non-toxic and non-flammable. In closed loop systems, internal substances are separate from the heat transport stream and can provide higher output temperatures than open systems in heating applications (Hauer, 2008). The charging process usually requires higher temperatures for closed rather than open systems (Hauer and Lavemann, 2007). A closed loop thermochemical TES system, with water is one of reactants, is illustrated as Figure 6.3, and an open loop thermochemical TES system in Figure 6.4.

The type of thermochemical system in terms of open or closed loop should be selected according to the design condition and properties of the system and thermochemical material.



**Figure 6.3. Charging (a) and discharging (b) process in closed thermochemical TES. Adapted from Edem et al. (2009).**



**Figure 6.4. Charging (a) and discharging (b) process in open thermochemical TES. Adapted from Hauer (2002).**

### 6.2.2.2 Thermochemical Material

Material selection is a key element that significantly affects the performance of thermochemical storage systems. Various materials can be used for compact storage systems. In order to achieve a significant understanding of the materials and their

properties, it is useful to draw on material science, solar and renewable energy, energy conservation, thermodynamics and reaction kinetics.

Key factors to be considered in selecting thermochemical material for a thermochemical storage system can be listed as follows (IEA-SHC, 2008; Edem et al., 2009):

- High storage density at the operating conditions
- Low charging time, which results in higher system efficiency as well
- Suitable availability
- High thermal conductivity and high heat transfer rate from material to heat exchangers, which increases the efficiency of the storage system
- Environmentally friendly, non toxic, non flammable (especially in open loop systems); low global warming potential (GWP) and ozone depletion potential (ODP)
- Non corrosive, which improves the effective life of components in thermochemical TES
- Low cost
- Good cyclic behavior (reversibility with little degradation over large numbers of cycles) as well as thermal and chemical stability under operating conditions (pressure and temperature)
- Ability to be engineered into a practical system (e.g., heat transfer characteristics and flow properties)
- Low temperature heat source required for the evaporation during discharging period
- Good reaction rate
- Moderate operating pressure range; no excessive pressure conditions

- Easy to handle and transport

In order to develop advanced materials for thermochemical storage systems, the following measures need to be accomplished (IEA, 2008):

- Identify, design and develop new composites and materials for thermochemical storage systems.
- Determine testing and measuring methods to determine the reliability of new storage materials.
- Determine the performance, stability and cyclic behaviour, and cost effectiveness of thermochemical materials and determine a method to predict the durability of the materials under repetitive cycles.

### **6.2.2.3 Cyclic Behavior of Thermochemical Materials**

The durability of thermochemical materials should be examined under repetitive cycles to demonstrate their operability. With an increasing number of thermochemical cycles, a thermochemical material degrades and its behaviour may change. The heat of dissociation (recovered heat) and the overall efficiency of the storage system may decrease over time and numbers of cycles.

A study has been performed by Kato et al. (1998) for a magnesium oxide/water reaction system for a heat pump and the durability of the materials under repetitive reactions has been investigated. Three types of MgO were chosen for the experiment: MgO material using ultra fine magnesium oxide powder as the precursor (UFP-Mg), MgO material using common magnesium hydroxide as the precursor (Com-Mg), and MgO using magnesium ethoxide as the precursor (Eth-Mg). 24 cycles of charging and discharging were performed on the three types of magnesium oxide

and UFP-Mg was found to have the highest durability and ability to avoid problems associated with repeated cycles.

Testing the materials helps assess whether there are significant difficulties with cyclability, degradation, heat transfer, etc.

#### **6.2.2.4 Cost**

Accurate determination and assessment of the major costs involved in a thermochemical storage plays a key role in a successful design. Total capital investment, operating and maintenance costs, and cost of the final products are important costs. In engineering projects, economic considerations should be combined with engineering economics for (Bejan et al., 1996):

- estimating total capital investment costs,
- evaluating the total product costs considering inflation, taxes, insurance, maintenance and operation costs, etc., and
- calculating the profitability of the system and performing comparisons with alternative investments.

In a thermochemical energy storage system, total capital costs include the cost of purchased equipment, e.g. reactors, the thermochemical material, heat exchangers, piping, structural and architectural work, electrical equipment and control systems, engineering and supervision, research and development, etc. In such systems, the total price is the price paid for the delivered thermal energy.

The total costs of thermochemical storage systems can be divided into two categories. Capital costs include total costs needed to bring a project to a commercially operable status such as the cost of construction and equipment. Operating costs include costs which are related to operation of the storage system.

Operating costs can be divided into two sub categories. Fixed costs include costs that do not vary depending on the volume of output. Variable costs which include costs that scale with the volume of output, e.g. materials, insurance, taxes, fuel, etc. The payback time is an important factor for evaluate economic viability and financial aspects of a project and to assist decision making.

Good cost estimation is an important part of thermochemical storage system design and plays an important role in the final decision making regarding the use of a design.

#### **6.2.2.5 Environment**

Thermochemical energy storage systems can reduce the overall environmental impact for a given application with considerable potential to limit contributions of energy systems to climate change. This can be achieved by enabling substitution for the fossil fuels conventionally used for energy systems. Consequently, pollution emissions related to conventional energy applications (mainly fossil fuel systems) can be reduced with thermochemical TES.

Generally, the environmental impacts to be considered consist of the human health and ecological impacts and resource depletion (Masruroh et al., 2006). Three important impacts are:

- Global warming potential (GWP)
- Acidification
- Eutrophication

These factors have been considered in an investigation by Masruroh et al. (2006) to evaluate the global warming potential (CO<sub>2</sub> equivalent), acidification (SO<sub>2</sub> equivalent), and eutrophication (phosphate equivalent) for a thermochemical system

combined with a solar energy system (called SOLARSTORE) using life cycle analysis (LCA). In the SOLARSTORE system a backup boiler is used to provide the excess heat requirements even though the use of conventional energy production produces emissions. Three conventional heating systems are considered in that study and compared with the SOLARSTORE system in terms of environmental impacts.

These systems are as follows:

- conventional solar heating system
- natural gas-based heating system
- low-sulphur oil-based heating system

The LCA results show that producing 1 GJ energy with the SOLARSTORE system results in global warming potential of 6.3-10 kg CO<sub>2</sub>, acidification of 46.6-70 g SO<sub>2</sub>, and eutrophication of 2.1-3.1 g phosphate. In order to compare these results with the three mentioned conventional systems, an annual heating requirement of 6800 kWh is assumed and the annum-based values of global warming potential, acidification, and eutrophication are evaluated for the SOLARSTORE and three conventional systems. The results show that thermochemical storage system provides a significantly superior solution for decreasing environmental impacts in comparison with the three traditional heating systems mentioned above. Table 6.1 shows the emissions reductions from using a thermochemical storage system in comparison with selected conventional energy systems.

**Table 6.1. Average annual reductions (in %) in environmental impacts using the SOLARSTORE system, in comparison with conventional heating systems.\***

Heating system	GWP	Acidification	Eutrophication
Conventional solar heating system	49.6	21.3	42.6
Natural gas	55.4	29.6	48.4
Low-sulphur heating oil	58.0	65.3	55.3

\* Adapted from Masruroh et al. (2006).

#### **6.2.2.6 Other Factors**

Along with above mentioned factors, other parameters should be considered in the design process of a thermochemical energy storage and to achieve an optimal design. These other factors include size of the storage system, safety and reliability of the overall system, maintenance, required trainings, etc.

### **6.3 Key Challenges in Designing a Thermochemical Storage System**

Designing a thermochemical energy storage system like any design process has some challenges that need to be investigated. Important challenges for such system can be investigated in four categories. These categories and their corresponding aspects are as follows:

#### a. Efficiency

- Achieving high efficiency (energy and exergy efficiency) at a satisfactory cost and in a marketable volume
- Achieving appropriate energy savings

#### b. Engineering

- Complicated concept in comparison with other types of TES as well as conventional energy systems
- Estimation of number of effective cycles and durability of thermal reliability of thermochemical materials
- Heat transfer process from materials to heat exchangers
- Lack of data and practical thermochemical storage systems

- Probable corrosions of the structure by materials and chemical reactions
- Lack of a general procedure to test the system performance
- Insulation at some points in the system with high possibility of heat losses

c. Economic

- Evaluation of capital and operating costs
- Estimation of payback time
- Assessment of lifetime of the system

d. Environmental

- Assessment of environmental impacts of thermochemical material and overall storage system

## **6.4 Key Developments Required for Designing a Thermochemical Storage System**

According to the complexities and difficulties related to designing a thermochemical storage system, some factors need to be considered further and some developments are required to overcome challenges and to achieve an appropriate method for designing a thermochemical storage system. These required developments for thermochemical TES are as follows (IEA, 2008):

- Find new composites and new combinations of materials suitable for thermochemical storage with lowest charging temperature and appropriate performance over time in chemical reversible interactions.
- Develop and apply standardised testing and validation methods for the performance, lifetime and safety of the storage system.

- Develop numerical models to understand and optimise the thermochemical behaviour and the overall storage system.
- Improve heat transfer rates from the thermochemical material to the heat exchanger walls.
- Assess the durability of components and determination of their long-term stability
- Assess the economic, environmental and technical feasibility of thermochemical TES.
- Assess the market potential of thermochemical TES.
- Identify where additional research is required.

# Chapter 7

## Parametric Study of Thermochemical Energy Storage Systems

### 7.1 Introduction

In order to understand the relation among various parameters affecting the performance of a thermochemical energy storage system, parametric analyses can be performed. As mentioned earlier, two of the most important parameters to assess the performance of a thermochemical storage system are its energy and exergy efficiencies. Various factors identified in the design section can influence both the energy and exergy efficiencies of a storage system. Each thermochemical energy storage is based on a working pair reaction for which the corresponding reaction has unique conditions, e.g. operating temperature and pressure, and enthalpy of reaction. Properties of thermochemical materials, e.g. durability and cyclic behavior, are other factors that have significant effects on the performance of thermochemical storage systems. Parametric analyses can be applied to investigate the effects of the above mentioned factors on system performance.

In this chapter, parametric studies are carried out for the thermochemical storage systems analyzed earlier in Chapters 4 and 5, to investigate the effects of selected parameters on the efficiency and behavior of thermochemical storage systems.

## 7.2 Effect of Charging Temperature on Efficiency

In this section the effects are examined of varying charging temperature on charging and overall energy efficiencies and exergy efficiencies.

### 7.2.1 Energy Efficiency

As mentioned in the design section, charging temperature can affect the overall efficiency of a thermochemical storage system. This effect is investigated for closed and open thermochemical energy storages, using previous illustrative examples. Energy efficiency is considered in this subsection and exergy efficiency subsequently.

#### 7.2.1.1 Closed Loop Thermochemical Energy Storage

In the closed loop thermochemical energy storage case study (described in section 4.4) the energy efficiencies of the charging and overall processes are dependent on the charging temperature. Specifically:

- Energy efficiency of the charging process:

$$\eta_c = \frac{\Delta H_{reaction}}{m_c C_p (T_1 - T_2)} \quad (7.1)$$

- Energy efficiency of the overall process:

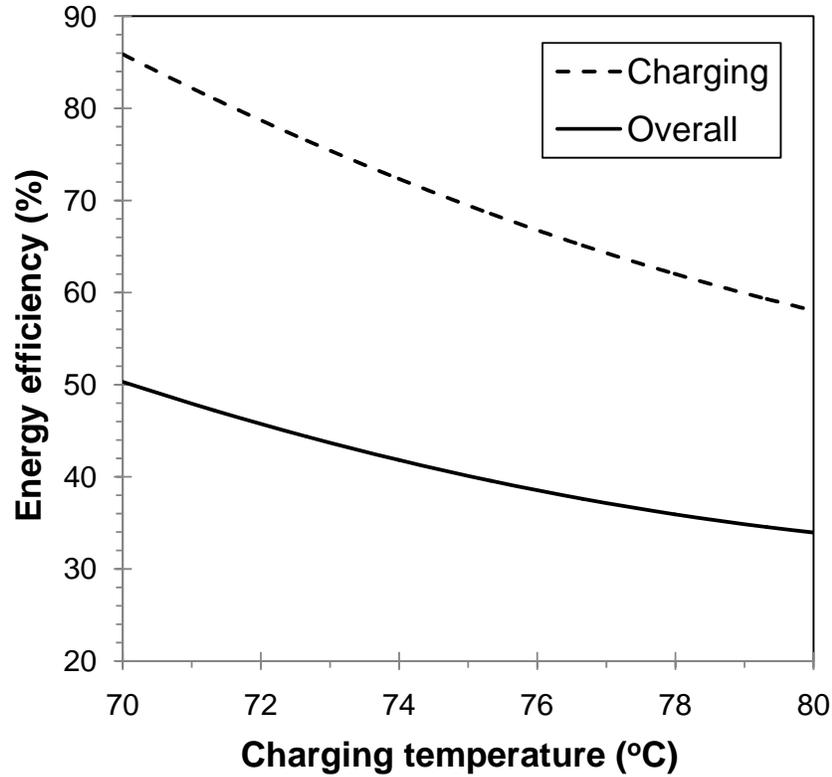
$$\eta_o = \frac{m_d C_p (T_4 - T_3)}{m_c C_p (T_1 - T_2)} \quad (7.2)$$

Here,  $T_1$  is the charging temperature supplied by solar energy (plate-type heat exchanger and flat collector panels). In efficiency calculations  $T_1$  has been assumed to be 70 °C but the maximum theoretical output temperature of the flat-plate solar collector can be 80 °C (Mauran et al., 2008). In this analysis  $T_1$  varies from 70 to 80 °C and other parameters are held constant in this analysis. So, the values of charging

and overall energy efficiencies relative to different values of  $T_1$  can be evaluated. The terms  $m_c$ ,  $m_d$ ,  $C_p$ ,  $T_2$ ,  $T_3$ ,  $T_4$  and  $\Delta H_{reaction}$  have been evaluated earlier as follows:

- $m_c = 14,866$  kg
- $m_d = 15,055$  kg
- $T_2 = 50$  °C
- $T_3 = 25$  °C
- $T_4 = 35$  °C
- $C_p = 4.183$  kJ/kg K
- $\Delta H_{reaction} = 3,732$  kJ/kg H<sub>2</sub>O

The effect of varying charging temperature on the charging and overall energy efficiencies is illustrated in Figure 7.1. This figure shows that the charging and overall energy efficiencies for the closed loop thermochemical TES case study decrease with increasing charging temperature. According to the results, magnitudes of charging and overall energy efficiencies are high with the increasing the charging temperature to 80 °C and they are 58% and 34% in 80 °C, respectively meaning that there is 32% reduction relative to their initial values.



**Figure 7.1. Charging and overall energy efficiencies vs. charging temperature in closed loop thermochemical TES case study.**

### 7.2.1.2 Open Loop Thermochemical Energy Storage

In the open loop thermochemical energy storage case study (explained in section 5.3), the energy efficiencies of the charging and overall processes are dependent on the charging temperature according to the following expressions:

- Energy efficiency of the charging process (due to lack of information about the enthalpy change of zeolite 13X dehydration process, we can use the general expression to evaluate the charging energy efficiency):

$$\eta_c = \frac{\Delta H_{ds}}{m_c C_p (T_1 - T_2)} = \frac{\text{useful output energy}}{\text{input energy}} \quad (7.3)$$

- Energy efficiency of the overall process:

$$\eta_o = \frac{Q_{recovered}}{m_c C_p (T_1 - T_2)} \quad (7.4)$$

Here,  $T_1$  is the charging temperature supplied by district heating system. In efficiency calculations  $T_1$  is assumed 130 °C but the maximum theoretical output temperature of the district heating system can be 180 °C (Hauer, 2002). In this analysis, the effect of varying charging temperature is considered and  $T_1$  varies from 130 to 180 °C. The effect of varying charging temperature on other parameters is neglected and as a result, other parameters are held constant. So, the values of charging and overall energy efficiencies relative to different values of  $T_1$  can be evaluated. The terms  $m_c$ ,  $C_p$ ,  $T_2$ , and  $Q_{recovered}$  have been evaluated previously as follows:

- $m_c = 60,240$  kg
- $T_2 = 40$  °C
- $C_p = 1.008$  kJ/kg K
- $Q_{recovered} = 4,110,073$  kJ
- *Useful input energy* = 5,040,000 kJ

Figure 7.2 shows the effect of varying charging temperature on the charging and overall energy efficiencies. This figure shows that varying the charging temperature in the open loop thermochemical TES case study has the same effect on the charging and overall energy efficiencies. The charging and overall energy efficiencies decrease with increasing charging temperature. According to the results, charging and overall energy efficiencies have acceptable values by increasing the charging temperature to 180 °C and they are 60% and 48%, respectively meaning that there is 35% reduction relative to their initial values.

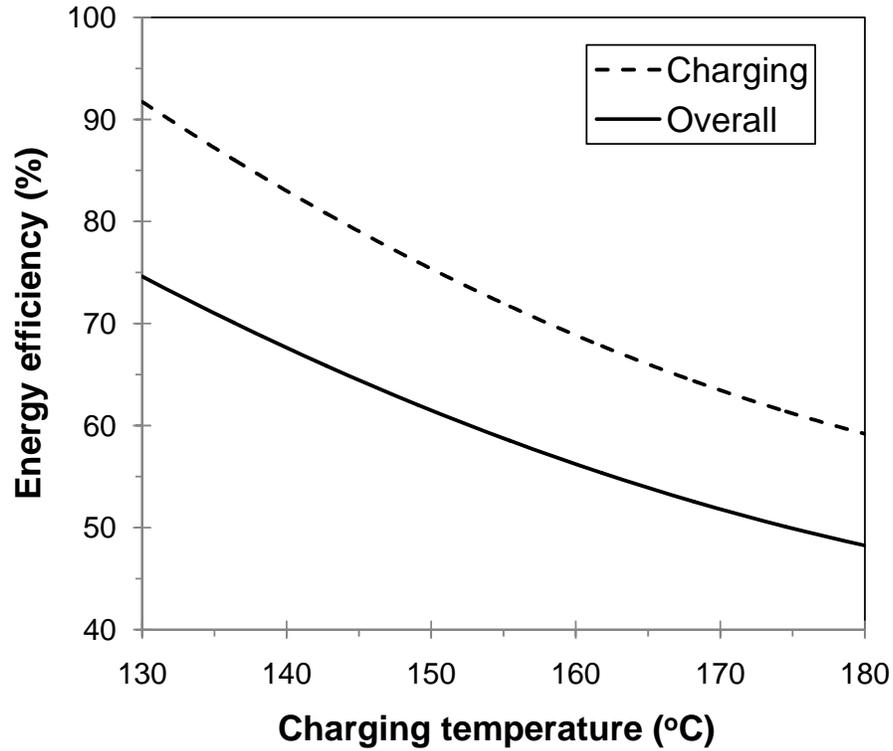


Figure 7.2. Charging and overall energy efficiencies vs. charging temperature in open loop thermochemical TES case study.

## 7.2.2 Exergy Efficiency

In this section, the effect of charging temperature on exergy efficiencies is investigated.

### 7.2.2.1 Closed Loop Thermochemical Energy Storage

In the closed loop thermochemical energy storage case study, the exergy efficiencies of the charging and overall processes are expressed as follows:

- Exergy efficiency of the charging process:

$$\psi_c = \frac{\text{Exergy stored in charging reaction}}{\text{Exergy input}} \quad (7.5)$$

- Exergy efficiency of the overall process:

$$\psi_o = \frac{\text{Exergy recovered}}{\text{Exergy input}} \quad (7.6)$$

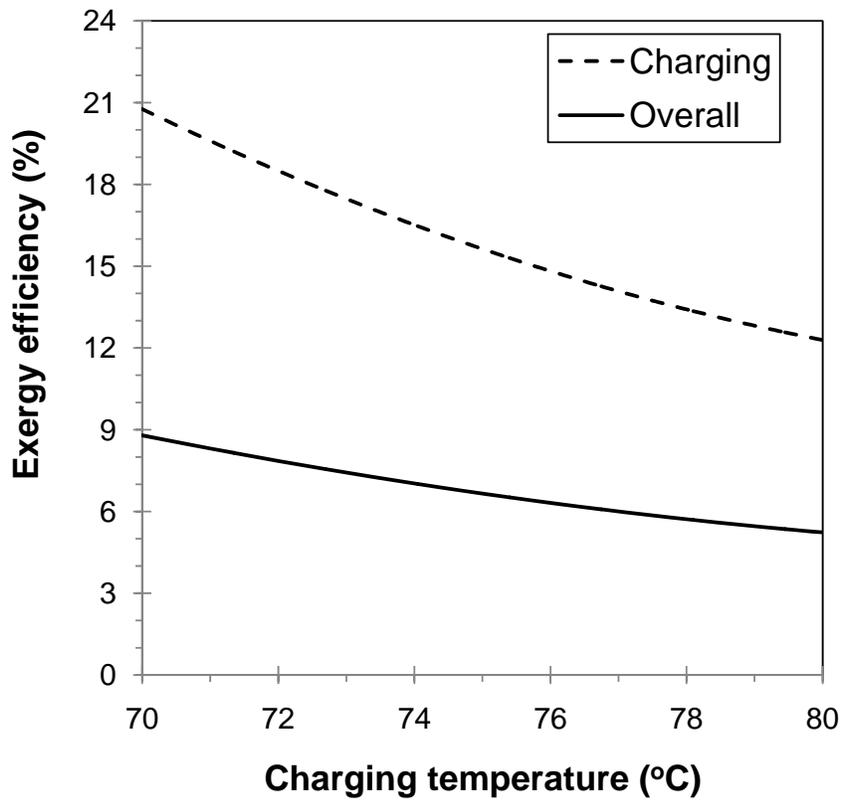
where,

$$\text{Exergy input} = m_c[h_1 - h_2 - T_0(s_1 - s_2)] \quad (7.7)$$

Here, the exergy stored and the exergy recovered have been calculated in section 4.4.3.2 and the exergy input is dependent on  $T_1$  because  $h_1$  and  $s_1$  are dependent on  $T_1$ . Values of the charging and overall exergy efficiencies for various values of  $T_1$  have been evaluated. Other parameters have been evaluated before as follows:

- $m_c = 14,866$  kg
- $T_0 = 25$  °C
- $T_2 = 50$  °C
- $h_2 = 209.4$  kJ/kg
- $s_2 = 0.7037$  kJ/kg K
- *Exergy stored in reaction* = 32,275.4 kJ
- *Exerg recovered* = 11,682.6 kJ

The effect of charging temperature on the charging and overall exergy efficiencies is illustrated in Figure 7.3. As shown in this figure, the charging and overall exergy efficiencies in closed loop thermochemical TES case study decrease with increasing the charging temperature. According to the results, the charging and overall exergy efficiencies of the storage system decreases 42% of its initial value by increasing the charging temperature to 80 °C which is a high reduction. The overall exergy efficiency reduction is not linear and will have a little reduction after 77 °C and this reduction will not reach zero.



**Figure 7.3. Charging and overall exergy efficiencies vs. charging temperature in closed loop thermochemical TES case study.**

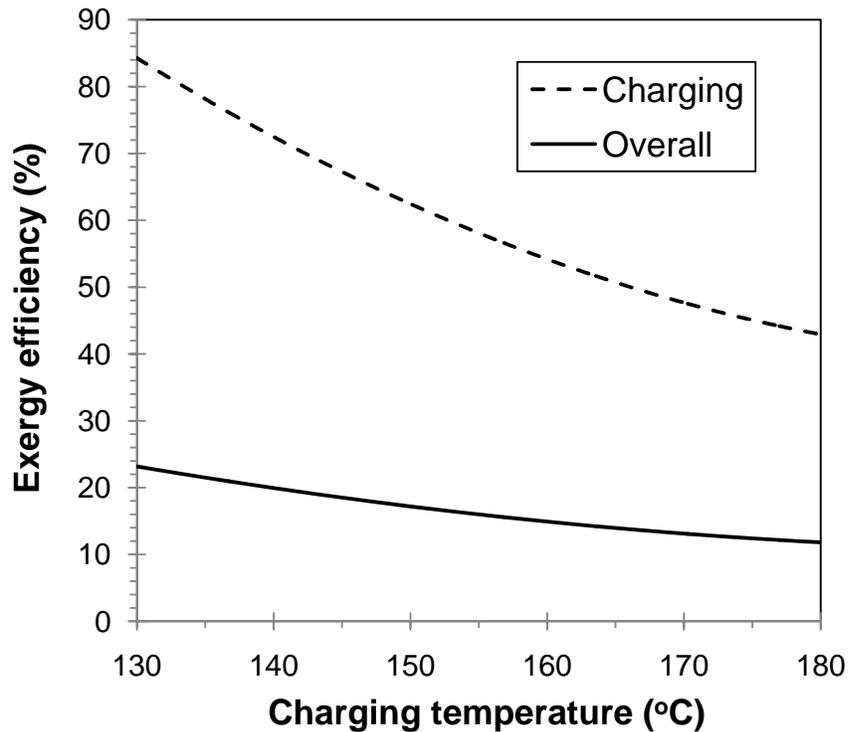
### 7.2.2.2 Open Loop Thermochemical Energy Storage

Using the same methodology for the open loop thermochemical energy storage case study, the charging and overall exergy efficiencies can be evaluated for various charging temperatures. Here, the exergy stored and the exergy recovered have been calculated and exergy input is dependent on  $T_1$  because  $h_1$  and  $s_1$  are dependent on  $T_1$ . Values of the charging and overall exergy efficiencies for various values of  $T_1$  can be evaluated. Other parameters have been evaluated before as follows:

- $m_c = 60,240$  kg
- $T_0 = 25$  °C
- $h_2 = 404.5$  kJ/kg

- $s_2 = 6 \text{ kJ/kg K}$
- *Exergy stored in desorption* = 794,847 kJ
- *Exergy recovered by air* = 218,696 kJ

The effect of varying charging temperature on the charging and overall exergy efficiencies for an open loop thermochemical TES using the system considered in the case study is illustrated in Figure 7.4. This figure shows that varying the charging temperature in the open loop thermochemical TES case study has the same effect on the charging and overall exergy efficiencies as the closed loop case study. The charging and overall exergy efficiencies decrease with increasing charging temperature. The charging and overall exergy efficiencies reduce 49% of their initial values with increasing the charging temperature to 180 °C.



**Figure 7.4. Charging and overall exergy efficiencies vs. charging temperature in open loop thermochemical TES case study.**

### 7.2.2.3 Summary

The effect of varying charging temperature on energy and exergy efficiencies of closed loop and open loop thermochemical TES case studies are summarized for selected temperatures in Tables 7.1 and 7.2.

**Table 7.1. Effect of charging temperature on charging and overall energy and exergy efficiencies of the closed loop thermochemical case study.**

Period	Efficiency type	Efficiency (%)	Charging temperature (°C)					
			70	72	74	76	78	80
Charging	Energy	$\eta_c$	86.1	79.2	72.7	67.0	62.3	58.1
Overall	Exergy	$\eta_o$	50.2	46.4	42.2	38.3	36.1	33.9
Charging	Energy	$\psi_c$	21.1	18.0	16.1	15.1	13.0	12.3
Overall	Exergy	$\psi_o$	8.8	7.9	7.0	6.4	5.7	5.1

**Table 7.2. Effect of charging temperature on charging and overall energy exergy efficiencies of the open loop thermochemical case study.**

Period	Efficiency type	Efficiency (%)	Charging temperature (°C)					
			130	140	150	160	170	180
Charging	Energy	$\eta_c$	92.1	83.4	75.0	68.9	64.5	59.6
Overall	Exergy	$\eta_o$	75.3	67.8	62.3	56.3	52.2	48.1
Charging	Energy	$\psi_c$	84.3	72.1	62.6	54.3	47.7	42.5
Overall	Exergy	$\psi_o$	23.2	19.8	17.2	15.0	13.1	11.7

### 7.3 Effect of Material Degradation on Efficiency

The degradation of the thermochemical storage material is an important design factor which affects the efficiency of such systems. Efficiency evaluations for the case studies are based on one complete cycle (charging, storing, and discharging) and it has

been assumed that all initial thermochemical material reacts in the charging reaction and after the discharging of the reaction, the thermochemical material is fully regenerated, i.e. it has its original mass and composition. Also it has been assumed that thermochemical material exhibits the same behavior and characteristics under repetitive storage cycles. In practice, a thermochemical material will degrade and lose its initial characteristics after a number of cycles. Reactivity and recovered heat are some characteristics that can decrease over time and with number of cycles (Sari and Karaipekli, 2009; Sari et al., 2004; Meeker et al., 1998; Cohen et al., 1980; Vantelon et al., 2005).

In this chapter, the effect of storage cycles on the energy and exergy efficiencies of the storage system is investigated for closed and open loop case studies. During a complete thermochemical storage cycle, a certain amount of heat/exergy is recovered after the discharging process. Due to degradation in chemical structure of thermochemical material, side reactions in the charging and discharging process, and the possible presence of impurities, the thermal stability of thermochemical material reduces after numbers of storage cycles. Therefore, the amount of recovered heat/exergy at the end of the discharging process will decrease. This means that the recovered heat/exergy for the next cycle is less than the corresponding amount for the previous cycle. Here, the term degradation refers to the reduction in the recovered heat/exergy after one storage cycle (charging, storing, and discharging).

### **7.3.1 Effect of Material Degradation on Energy Efficiency**

Due to lack of experimental data related to the effect of material degradation and cyclic behavior on the recovered heat of closed loop and open loop thermochemical

storage systems, experimental data taken from some latent TES systems are used here. The thermal stability of PCMs in latent TES systems have been investigated by many authors and the latent heat storage capacity of corresponding systems have been measured. Sari and Kaygusuz (2003) investigated the thermal stability of some fatty acids as phase change material. The selected PCMs were stearic, palmitic, myristic, and lauric acid. The latent heat storage capacity of these PCMs was measured after a short term period (40 cycles), middle-term period (410 cycles), and long-term period (910 cycles). The results showed that latent storage capacity of stearic, palmitic, myristic, and lauric acid reduced after each thermochemical cycle and the average reduction after each cycle is 0.2%, 0.3%, 0.15% and 0.5%, respectively.

In this study, four values of this reduction of the recovered heat are assumed; 0.3% and 0.5% of the recovered heat after each thermochemical cycle which these values are similar to PCMs. Since the actual values for degradation of the recovered heat are not known, two larger values, 1% and 3%, are assumed. In this regard, the recovered heat after each thermochemical cycle is calculated using the following expression:

$$Q_{recovered,n+1} = [Q_{recovered,n} - \left(\frac{x}{100} Q_{recovered,n}\right)] \quad (7.8)$$

Here,  $Q_{recovered}$  denotes the recovered heat after each thermochemical cycle and  $n$  is the number of thermochemical storage cycle and  $x$  is the reduction percentage per each cycle. Values of  $n$  and  $x$  are as follows:

- $n = 1, 2, \dots, \dots, 400$
- $x = 0.3, 0.5, 1, 3$

### 7.3.1.1 Closed Loop Thermochemical Energy Storage

The recovered heat is the amount of heat released after the discharging process and used for heating purposes, e.g. domestic hot water and space heating. A change of the recovered heat affects the overall energy efficiency according to the following expressions:

- Energy efficiency of the overall process:

$$\eta_o = \frac{Q_{recovered}}{Q_{input}} \quad (7.9)$$

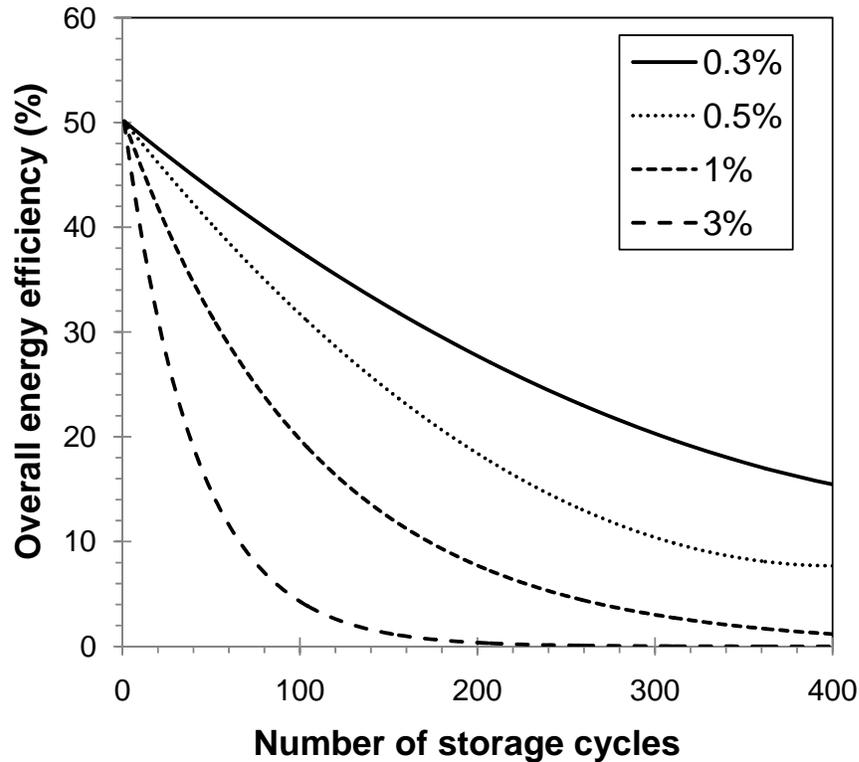
Here,  $Q_{recovered}$  is the recovered heat after one thermochemical cycle and  $Q_{input}$  is the input heat to the storage system during the charging process. The recovered energy  $Q_{recovered}$  for the first thermochemical cycle and the net input energy  $Q_{input}$  have been calculated before as follows:

- $Q_{recovered} = 629,750$  kJ
- $Q_{input} = 1,243,689$  kJ

Material degradation can be assumed to occur after repetitive cycles and to reduce the recovered heat. So, in this study the recovered heat varies over numbers of cycles and the input heat is held constant and, as a result, the overall energy efficiency of closed loop thermochemical TES varies over numbers of thermochemical cycles.

The effect of degradation of the recovered heat on the overall energy efficiency of the storage system is shown in Figure 7.5. In this figure, four percentages have been assumed for the recovered heat reduction after each thermochemical cycle and the overall energy efficiency of the storage system has been plotted versus number of storage cycles. According to Figure 7.5, the overall energy efficiency of the closed loop thermochemical TES case study decreases with increasing the number of storage cycles. As it can be seen from the figure, the overall

energy efficiency of the storage cycle with 0.3% degradation has acceptable value during 400 storage cycles and after 250 cycles the overall energy efficiency reduces 50% of its initial value. With 0.5%, 1%, and 3% degradation, the overall energy efficiency reduces 50% after 160, 80, and 40 storage cycles, respectively.



**Figure 7.5. Overall energy efficiency vs. number of cycles for closed loop thermochemical TES with 0.3%, 0.5%, 1% and 3% reduction in recovered heat after each cycle.**

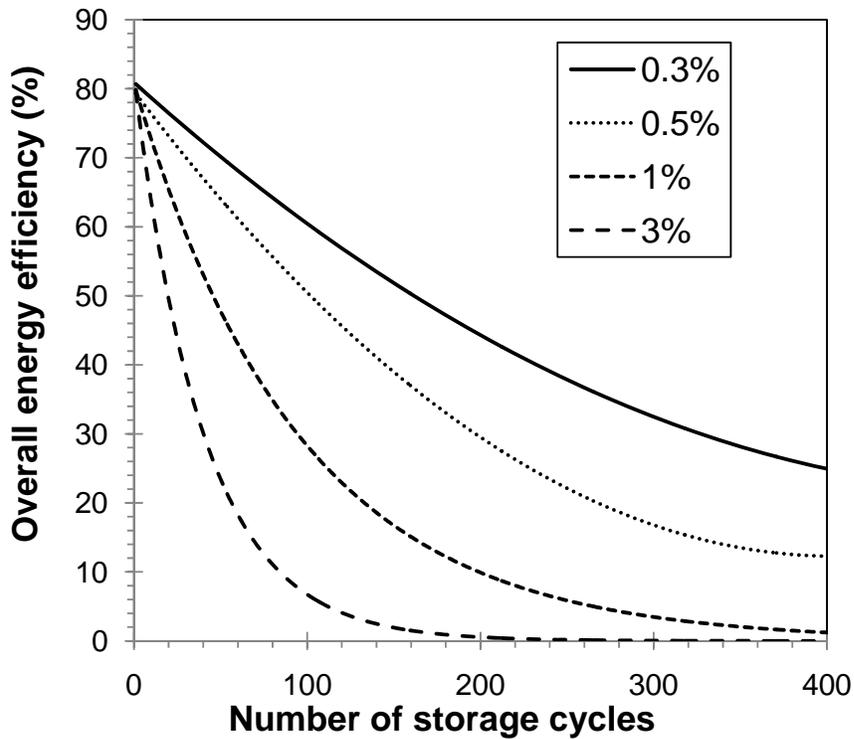
### 7.3.1.2 Open Loop Thermochemical Energy Storage

Using the same methodology with section 7.3.1.1 for the closed loop case study, the effect of degradation of the recovered heat on the overall energy efficiency of the open loop thermochemical TES storage system can be investigated (see Figure 7.6). Figure 7.6 shows that the overall energy efficiency of the open loop thermochemical TES case study decreases with increasing the number of storage cycles. The recovered

heat  $Q_{recovered}$  for the first thermochemical cycle and  $Q_{input}$  have been calculated before as follows:

- $Q_{recovered} = 4,110,073$  kJ
- $Q_{input} = 5,040,000$  kJ

According to Figure 7.6, the overall energy efficiency decreases with increasing the number of storage cycles. As it can be seen from the figure, the overall energy efficiency of the storage cycle with 0.3% degradation has acceptable value during 400 storage cycles and after 260 cycles the overall energy efficiency reduces 50% of its initial value. With 0.5%, 1%, and 3% degradation, the overall energy efficiency reduces 50% after 160, 80, and 40 storage cycles, respectively.



**Figure 7.6. Overall energy efficiency vs. number of cycles for open loop thermochemical TES with 0.3%, 0.5%, 1% and 3% reduction in recovered heat after each cycle.**

### 7.3.2 Effect of Material Degradation on Exergy Efficiency

Exergy is the energy that is available to be used and according to Dincer and Rosen (2007) domains of energy and exergy have an intersection field which in this field the exergy is a subset of energy. Here, illustrative examples possess energy and exergy and appear at this intersection. Thus, it can be assumed that the degradation in the recovered exergy is proportional to the energy degradation. Using the same methodology with the energy efficiency analysis in the section 7.3.1, four values, 0.3%, 0.5%, 1% and 3% are assumed for reduction of the recovered exergy after each thermochemical cycle and the effect of this degradation on overall exergy efficiency is considered.

#### 7.3.2.1 Closed Loop Thermochemical Energy Storage

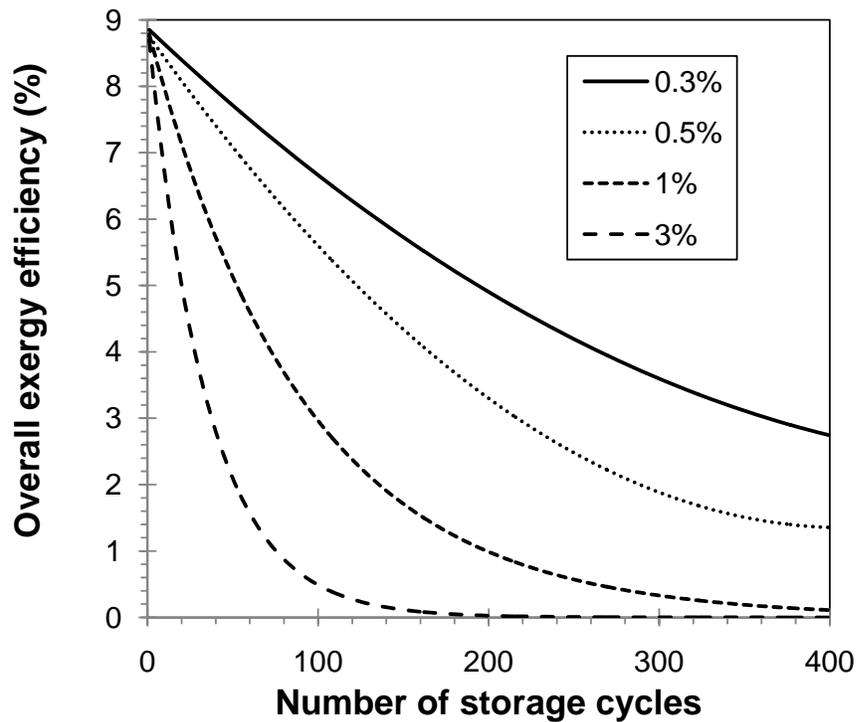
The effect of degradation of the recovered exergy on the overall exergy efficiency of the closed loop thermochemical TES storage system is investigated. In the closed loop thermochemical energy storage, the exergy efficiency of the overall process is expressed with the following expression:

$$\psi_o = \frac{\epsilon_{recovered}}{\epsilon_{input}} \quad (7.10)$$

Here,  $\epsilon_{recovered}$  is the recovered exergy after one thermochemical cycle and  $\epsilon_{input}$  is the input exergy to the storage system during the charging process. The recovered exergy  $\epsilon_{recovered}$  for the first thermochemical cycle and the net input exergy  $\epsilon_{input}$  have been calculated earlier as follows:

- $\epsilon_{recovered} = 11,682 \text{ kJ}$
- $\epsilon_{input} = 129,807 \text{ kJ}$

The effect of degradation of the recovered exergy on the overall exergy efficiency of the storage system is shown in Figure 7.7. Analogously with the section 7.3.1.1, the recovered exergy varies over numbers of cycles and the input exergy is held constant. As a result, the overall exergy efficiency of closed loop thermochemical TES decreases as the number of thermochemical cycles increases. As it can be seen from the figure, the overall exergy efficiency of the storage cycle with 0.3% and 0.5% degradation is in an acceptable range during 280 and 150 storage cycles, respectively. With 1% and 3% degradation, the overall exergy efficiency has acceptable value only during the first 90 and 40 storage cycles, respectively.



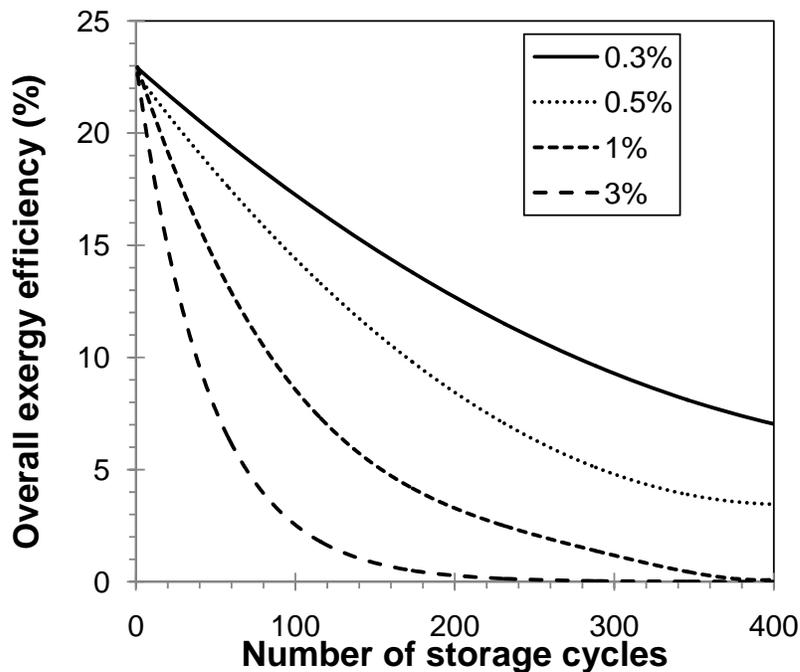
**Figure 7.7. Overall exergy efficiency vs. number of cycles for closed loop thermochemical TES with 0.3%, 0.5%, 1% and 3% reduction in recovered exergy after each cycle.**

### 7.3.2.2 Open Loop Thermochemical Energy Storage

Using the same methodology with the closed loop system, the effect of degradation of the recovered exergy on the overall energy efficiency of the storage system is shown in Figure 7.8. The recovered exergy  $\epsilon_{recovered}$  for the first thermochemical cycle and the net input exergy  $\epsilon_{input}$  have been calculated before as follows:

- $\epsilon_{recovered} = 218,696$  kJ
- $\epsilon_{input} = 942,635$  kJ

The overall exergy efficiency decreases with increasing the number of storage cycles in the open loop thermochemical TES case study. As shown in Figure 7.8, the overall exergy efficiency of the storage cycle with 0.3% and 0.5% degradation is in an acceptable range during 250 and 150 storage cycles, respectively. With 1% and 3% degradation, the overall exergy efficiency has acceptable value only during the first 90 and 40 storage cycles, respectively.



**Figure 7.8. Overall exergy efficiency vs. number of cycles for open loop thermochemical TES with 0.3%, 0.5%, 1% and 3% reduction in recovered exergy after each cycle.**

## 7.4 Discussion

The parametric studies performed in this chapter describe quantitatively the effects charging temperature and material degradation on efficiencies by utilizing illustrative examples.

The effect of varying charging temperature on the overall energy and exergy efficiencies is shown in Figures 7.1-4. The results show that the charging and overall energy and exergy efficiencies for both closed and open loop systems decrease by increasing the charging temperature. Comparing the results between energy and exergy efficiencies in closed and open loop case studies shows that the charging and overall energy/exergy of the closed loop case study has less reduction relative to the corresponding efficiencies in the open loop case study. Furthermore, exergy efficiencies (charging and overall) in both case studies have more reduction relative to the corresponding energy efficiencies.

The effect of material degradation on efficiencies relative to 400 thermochemical cycles has been studied. Here, degradation refers to the reduction of the recovered energy/exergy after each thermochemical cycle and is assumed to reduce 0.3%, 0.5%, 1%, and 3% after each storage cycle. Comparing the results shows that the overall energy and exergy efficiencies of both closed loop and open loop storage systems have the same reduction rate and these efficiencies decrease to 50% of their initial values after about 250, 160, 80, 40 storage cycles with 0.3%, 0.5%, 1%, and 3% degradation, respectively.

Depending on the expected efficiency from the storage system and durability of thermochemical material over number of cycles, thermochemical materials need to be renewed in thermochemical TES storage systems. Thermochemical materials can be replaced after specific number of cycles according to projected efficiencies and

economical aspects. If the expected efficiency is high and the cost of thermochemical materials is low, to avoid decreasing the overall energy and exergy efficiencies of the storage system due to material degradation, thermochemical materials can be renewed after short periods of storage cycles.

Charging temperature and material degradation over number of thermochemical cycles are of important parameters in designing a thermochemical energy storage system. Achieving appropriate efficiencies and sufficient development of material durability are key factors in enhancing thermochemical storage systems and in optimizing designs.

# Chapter 8

## Conclusions and Recommendations

### 8.1 Principle Findings

In this thesis, a comprehensive review of various types of TES systems, highlighting thermochemical TES, has been investigated. The key important findings of this research are as follows:

- TES can help achieve substantial efficiency, environmental and economic benefits.
- 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.
- Comprehensive analyses of thermochemical TES 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.

### 8.2 Conclusions

The main conclusions of this study are as follows:

- Thermochemical storage system is a promising technology for storing thermal energy for later utilization. They are undergoing research and experimentation and further research is needed to improve understanding of thermochemical TES.

- Integrating TES with HVAC systems results in reducing electrical power consumption and increasing the system COP.
- Exergy analysis can assist efforts to improve or optimize design. The use of exergy analysis is a key factor to compare efficiencies of TES systems and improve them by specifying reasons and locations of thermodynamic losses in various processes of TES systems.
- The design of thermochemical TES systems is complex and requires consideration on many factors, e.g., economic, efficiency, environmental, and engineering aspects. Selecting thermochemical materials, considering market potential, systems design e.g. reactor concepts and closed/open loop systems, are some examples of these factors.
- Charging temperature and material degradation can affect the energy and exergy efficiencies of the storage system and efficiencies decrease with increasing number of thermochemical cycles and charging temperature.

### **8.3 Recommendations**

The recommendations for this study that were made in Chapters 1 to 7 are summarized in this section. According to this work, further research is recommended to improve understanding of the scientific and engineering characteristics of thermochemical TES systems and to help develop various aspects relating to the performance and implementation of these systems. In order to select a TES system for an HVAC application, it is recommended to consider factors e.g. environmental, economic, operating, sizing, and reliability. In this study, due to lack of experimental data, the degradation amount of thermochemical material over time has been assumed. It is recommended to experimentally evaluate the actual degradation amount of

thermochemical materials of the mentioned case studies. Along with the actual material degradation amount, the cost of thermochemical material is another important factor related to the thermochemical material. As it has been shown in Chapter 7, efficiencies of the storage systems reduce after number of thermochemical cycles and according to the projected efficiencies, thermochemical material should be replaced. Decision making about replacing thermochemical can be performed considering these factors with more accuracy.

In order to improve various design aspects relating to the performance and implementation of thermochemical TES systems, some recommended developments for future research are presented as follows:

- The thermochemical material is a critical component of such systems. The cyclic behavior and degradation of thermochemical materials, as well as their cost, availability, environmental effects, durability, reliability of the overall system, and energy density, are important parameters affecting the selection of a thermochemical material. Feasibility studies that consider these factors for specific applications appear to be merited.
- Find new composites and new combinations of materials suitable for thermochemical storage.
- Develop and apply standardised testing and validation methods for the performance, lifetime and safety of the storage system.
- Develop numerical models to understand and optimise the thermochemical behaviour and the overall storage system.
- Perform exergoeconomic analysis for thermochemical TES systems.

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