

STORAGE OF THERMAL ENERGY BY CHANGE OF PHASE

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Contents

1. Introduction
 2. Phase Change Thermal Energy Storage Systems
 - 2.1 Major Design Features
 - 2.2 Selection of the Phase Transition
 - 2.3. Phase Change Materials (PCMs)
 - 2.3.1. Selection of the PCM
 3. The Thermodynamic Analysis of a Phase Change Thermal Energy Storage System
 - 3.1 Description of the System to Be Analyzed
 - 3.2 Assumptions for the Analysis
 - 3.3 Development of the Analytical Model
 4. Results
 5. Conclusions and Recommendations
- Glossary
Bibliography
Biographical Sketch

Summary

This chapter examines the design and operation of phase change thermal energy storage systems.

A thermodynamic analysis of a generic system is used to illustrate the major advantages of phase change systems over sensible heat systems; namely, smaller size and weight. Design criteria for phase change systems are discussed and a brief review of phase change materials is presented.

1. Introduction

When the supply of and demand for thermal energy are asynchronous, some provision for storage often improves the economics of operating an energy conversion system. A wide spectrum of opportunities exists for employing thermal energy storage systems in industrial-, residential-, and commercial-scale applications such as space and water heating and the operation of manufacturing processes.

There is also a newly emerging role for thermal energy storage in the deregulated and restructured electricity generation industry.

Independent of the specific application of interest, a thermal energy storage system may be characterized by specifying factors such as the capacity of the system, the rapidity at which the system can deliver thermal energy to the load, the storage medium employed, and the range of temperatures at which energy is stored.

Thermal energy storage systems may be classified as either sensible heat systems, in which a temperature change can be sensed when energy is stored or released, or as latent heat systems; which include systems based on a phase change, the heat of reaction in a reversible chemical reaction, or the heat of adsorption/desorption. This chapter is focused on the design and operation of phase change thermal energy storage systems.

2. Phase Change Thermal Energy Storage Systems

2.1 Major Design Features

A typical phase-change thermal energy storage system is composed of three major types of components: the storage elements, a heat exchanger for transferring heat from a hot stream of fluid to the storage elements and from the storage elements to a cold stream of fluid, and fans, pumps, or blowers to maintain the flows of these streams through the storage elements. Phase-change energy storage systems store most of the thermal energy as the latent heat of fusion of a phase change material (PCM).

Thus, the energy is stored at the constant phase transition temperature of the PCM used in the storage elements. A PCM commonly has a latent heat that is as much as two orders of magnitude larger than the amount of energy required to heat a unit mass of either phase in the transition through a unit change of temperature. For example, palmitic acid is a PCM which has a latent heat of fusion of approximately 200 kJ kg^{-1} , while it takes approximately 2.2 kJ kg^{-1} to heat a unit mass of the acid through a sensible temperature change of $1 \text{ }^\circ\text{C}$. Thus, a phase change energy storage system requires a much smaller weight and volume to store a given amount of energy than does a comparable sensible heat storage system.

The high energy storage density of a phase change system is considered to be its major advantage. This feature is especially important in applications such as residential and spacecraft storage systems, in which minimizing the weight and/or volume of the storage system is an important factor.

2.2 Selection of the Phase Transition

In general, an engineer designing a phase change thermal energy storage system is free to choose a design based on a solid-solid (A solid like ice or iron can have one or another crystal structure depending on the pressure and temperature applied to it. Changing from one structure to the other is a type of phase change and it involves energy release or absorption.

However such energy exchanges in connection with solid to solid phase change are very small in comparison to solid – liquid and liquid – vapor phase change.), liquid-gas, solid-gas, or solid-liquid phase transition.

A paucity of suitable PCMs has virtually eliminated the use of solid-solid phase transitions in practical designs. Although liquid-gas PCMs commonly have large heats of vaporization, they are seldom used since they involve changes in volume that are so large that they negate the principal advantage of a phase change thermal energy storage system: the high energy storage density.

PCMs that use a solid-gas phase transition are also eliminated for the same reason. Solid-liquid PCMs can store comparatively large amounts of thermal energy over a narrow range of temperatures with only insignificant changes in the volume occupied by the storage element. Thus, the designs of most storage elements are based on the use of a solid-liquid phase transition.

2.3. Phase Change Materials (PCMs)

2.3.1. Selection of the PCM

The selection of an appropriate phase change material is one of the most important decisions that must be made by the designer of a phase change thermal energy storage system. The major categories of these materials include salt hydrates, paraffins, non-paraffin organics, eutectics, and salt mixtures. The characteristics of PCMs in each of these categories are discussed below. The applicable temperature ranges for a number of PCMs are shown in Table 1.

Temperature Range, (°C)	Phase Change Material	Transition Temperature, (°C)
0 - 100	Water	0
	Paraffin	20 – 60
	Salt Hydrate	30 – 50
100 - 400	AlCl ₃	192
	LiNO ₃	250
	Na ₂ O ₂	360
400 - 800	50LiOH/50LiF	427
	KClO ₄	527
	LiH	699
800 - 1500	LiF	868
	NaF	993
	MgF ₂	1271
	Si	1415

Table 1: PCMs and Their Temperature Ranges

2.3.1.1. Salt Hydrates

Many salt hydrates such as Glauber's salt (sodium sulfate decahydrate), calcium chloride hexahydrate, sodium acetate trihydrate, sodium thiosulfate pentahydrate, and barium hydroxide octahydrate have been proposed for use as PCMs. These materials are attractive because of their relatively low costs; however, they should not be used without addressing their attendant problems with supercooling and phase segregation.

Techniques such as the addition of nucleating agents, or the promotion of nucleation by roughening container walls or heat transfer to cold extended surfaces have been used to combat supercooling.

Phase segregation can be prevented by the use of thickening agents or rotating storage devices. Encapsulation of PCMs in plastic or metal containers has also been used to mitigate phase segregation. The use of metals, especially mild steel, for encapsulation can cause corrosion problems if the steel is not properly coated to prevent direct contact with a salt hydrate PCM. The least expensive PCM containers have proven to be plastic bottles and tin plated steel cans.

2.3.1.2. Paraffins

Paraffins, which are petroleum derivatives, possess many attributes that make them excellent candidates for use as PCMs. They are economical, have a high heat of fusion, a low vapor pressure in the melt, exhibit negligible supercooling and no phase segregation, and are chemically stable and inert. They also display some undesirable characteristics such as a low thermal conductivity and a large volume change during the liquid-solid phase transition.

The low thermal conductivity has been overcome by techniques such as the use of extended heat transfer surfaces and the addition of aluminum particles to improve the effective thermal conductivity. Pure (laboratory grade) paraffins are too expensive to use as PCMs in thermal energy storage systems. Thus, in practical systems engineers commonly specify the use of so-called technical grade paraffins. Since technical grade paraffins are not pure, but are composed of a mixture of hydrocarbons, they exhibit a range of melting temperatures as opposed to a single value.

Furthermore, the thermo-physical properties of paraffins published by their manufacturers are typically representative of laboratory rather grade materials rather than the technical grade materials actually used in real systems. Thus, it has been suggested that designers measure the thermo-physical properties of the technical grade PCM that they will use in their system instead of relying on the manufacturer's data.

2.3.1.3. Non-Paraffin Organics

This category of PCMs includes esters, fatty acids, alcohols, and glycols. These materials have melting points from approximately 5 °C to 190 °C and heats of fusion in the range of 40 to 250 (kJ/kg). The fatty acids have excellent melting/freezing properties and do not present any problems with supercooling. They are, however, about three times more costly than paraffins and do present some materials compatibility problems.

2.3.1.4. Eutectics

Eutectic PCMs are mixtures of two or more salts that have specific phase transition temperatures. They are classified as inorganic, organic, or organic-inorganic eutectics. The melting point and heats of fusion of a number of eutectics are listed in Table 2.

Inorganic Eutectics	Melting Point (°C)	Latent Heat Of Fusion (kJ/kg)
49.3% MgCl \cdot 6H $_2$ O + 50.7% Mg(NO $_3$) $_2$ \cdot 6H $_2$ O	58	132.3
Na $_2$ SO $_4$ (32.5%)H $_2$ O (41.4%), NaCl (6.66%), NH $_4$ Cl (6.16%)	13	146
61.5% Mg(NO $_3$) $_2$ \cdot 6H $_2$ O + 38.5% NH $_4$ NO $_3$	51	131.3
58.3% Mg (NO $_3$) $_2$ \cdot 6H $_2$ O + 41.7% MgCl $_2$ \cdot 6H $_2$ O	58	106
CaCl $_2$ \cdot 6H $_2$ O + CaBr $_2$ \cdot 6H $_2$ O	14	140
Organic Eutectics		
Lauric-capric acid	18	120
Lauric-palmitic	33	145
Lauric-stearic	34	150
Palmitic-stearic	51	160

Table 2: Eutectic Phase Change Materials

2.3.1.5. Salt Mixtures

Salt/ceramics comprise a relatively new class of storage element media that are still under development. These materials encapsulate a PCM in the submicron pores of a ceramic matrix. Surface tension forces retain the liquid salt PCM within the pores of a solid ceramic.

Energy is stored in the PCM/ceramic composite as a combination of the latent heat of the PCM and the sensible heating of the solid ceramic. A similar approach has been taken to impregnate a PCM in gypsum wallboard to enhance the thermal energy storage capacity of buildings.

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Biographical Sketch

Robert J. Krane received a bachelor's degree in Aeronautics at St. Louis University / USA in 1959 and joined McDonnell Aircraft. From 1960-62 he worked on the propulsion performance analysis of the Saturn, Atlas, and Centaur rockets at NASA-Marshall in Huntsville, Alabama and then returned to school at the University of Illinois (Urbana) where he obtained his Bachelor of Science in mechanical engineering in 1963. After working from 1963 through 1968 for Douglas Aircraft on Saturn and Skylab projects and completing a Master of Science at the University of Southern California he went on to the University of Oklahoma for his doctorate on natural convection, which he completed in 1972. Then he joined the faculties at Oscar Rose College (1972-74), West Virginia University (1974-76) and the University of Tennessee (1976-2003). He has many scientific publications. He died in 2003.