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Thermal Energy Storage by Using Latent Heat Storage Materials

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Abstract— Many renewable energy sources are not available at any time in nature and some energy sources is reducing so the development of energy storage technologies is very important to converse the available energy and improve its utilization. The use of a phase change material (PCM) is a very promising technology for thermal energy storage. Classification of phase change materials are presented. The geometry of phase change material (PCM) container is considered one of the required important factors. Thermal energy storage is used in many engineering applications such as space heating and air conditioning, solar water heating and waste heat recovery systems.

Index Terms- Thermal Energy Storage, Latent heat storage, Phase change materials (PCM), Organic and Inorganic materials, PCM containers.

1 Introduction

The development of energy storage technologies is very important to converse the available energy and improve its utilization, since many energy sources are not available at any time in nature and some energy sources is reducing. Thermal energy storage is used in these technologies. Most applications use Short term storage of only a few hours; however, some applications are required in long term storage systems of a few months. The different ways of storing energy are mechanical, electrical, thermal energy and thermo chemical energy storage [1-2].

Solar energy systems require efficient thermal energy storage to store the heat during sunshine hours and using the heat stored during the night. Thermal energy storage is very important in many engineering applications such as space heating and air conditioning, solar cooking, greenhouses, solar water heating and waste heat recovery systems. For example: domestic space heating and air conditioning leads to variation in electrical energy consumption during the day and night. Such variation leads to an off peak period, usually after midnight until early morning. Accordingly, power stations have to be designed for capacities sufficient to meet the peak load. Otherwise, very efficient power distribution would be required. Better power generation management can be achieved if some of the peak load could be shifted to the off peak load period, which can be achieved by thermal storage of heat or coolness. Hence, the successful application of load shifting and solar energy depends to a large extent on the method of energy storage use [3-16].

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2. Energy Storage Methods

The different ways of storing energy are mechanical, electrical, thermal energy, and thermo chemical energy storage [1, 2].

2.1 Mechanical Energy Storage

Mechanical energy can be stored in a number of ways in order to use it at a later date, usually in the form of kinetic energy or momentum. Mechanical energy storage systems such as flywheels, or pumped hydropower storage (PHPS) and compressed air energy storage (CAES) .the flywheel can give or receive rotational energy in times of need and it is more suitable for intermediate storage.

Hydropower storage is carried out at night, when electricity rates are much less expensive; pumps are used to pump water from a lower elevation to a higher elevation. This hydro storage can be used to run turbines and generate electricity when power is needed because of insufficient supply from the base-load plant. Compressed air storage works in a similar way; when electricity demand is low; air is compressed into a storage tank, and is used to run turbines during high demand times. The PHPS and CAES technologies can be used for large-scale utility energy storage.

2.2 Electrical Storage

The applications of electrical storage types are very important in the world today. Capacitors, for example, are devices that can store energy in the electric field between two charged

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plates. They are more commonly used in electronic devices to keep a more constant power supply, while a battery is being charged by connecting it to a source of direct electric current and when it is discharged the stored chemical energy is converted into electrical energy. The most common type of storage batteries is the lead acid and Ni–C d. Potential applications of batteries are utilization of off-peak power, load leveling, and storage of electrical energy generated by wind turbine or photovoltaic plants.

2.3 Thermal Energy Storage

Thermal energy storage (TES) can be stored in of two ways: latent and/or sensible storage. Different types of thermal storage are shown in Figure1.

2.3.1 Sensible Heat Storage

Sensible thermal storage is the energy stored in a change in temperature of a material. SHS system utilizes the change in temperature of the material during the process of charging /discharging and the heat capacity or a specific heat, which means the amount of energy it takes to change the temperature of one kilogram of a substance by one degree. The amount of heat stored depends on the specific heat of the medium, the temperature change and the amount of storage material.

$$Q = \int_{T_i}^{T_f} mC_p dT = mC_{ap}(T_f - T_i) \quad (1)$$

The main disadvantage of sensible TES is its large storage size. For example, freezing just one kilogram of ice will absorb 334 kJ of energy. The best SHS liquid available is Water because it is cheap and has a high specific heat. However above 100 °C, oils, molten salts and liquid metals, etc. are used. The rock bed type storage materials are used for air heating applications [2].

2.3.2 Latent Heat Storage

Latent heat is the heat released or absorbed by a body during a change of state without change of temperature, say from liquid to solid (as ice freezes) or from a liquid to a gas (as water boils) [2]. The storage capacity of the LHS system with a PCM medium is given by

$$Q = \int_{T_i}^{T_m} mC_p dT + ma_m \Delta h_m + \int_{T_m}^{T_f} mC_p dT \quad (2)$$

$$Q = m[C_{sp}(T_m - T_i) + a_m \Delta h_m + C_{lp}(T_f - T_m)] \quad (3)$$

Latent heat storage system is an effective way of storing thermal energy and has the advantages of high-energy storage density and its characteristics to store heat at constant temperature corresponding to the phase- transition temperature of phase change material (PCM). Phase change can be in the following form: solid–solid, solid–liquid, solid–gas, and liquid–gas and vice versa.

The advantages of solid–solid PCMs are less stringent container requirements and greater design flexibility. Solid–solid transitions have small latent heat and small volume changes than solid–liquid transitions. Most promising materials are organic solid solution of pentaerythritol (m .p. 188 °C, latent heat of fusion 323 kJ/kg), pentaglycerine (m .p. 81 °C, latent heat of fusion 216 kJ/kg), Li_2SO_4 (m .p. 578, latent heat of fusion 214 kJ/kg) and KHF_2 (m .p. 196 °C, latent heat of fusion 135 kJ/kg) . Trombe wall with these materials could provide better performance than a plain concrete Trombe wall.

Solid–gas and liquid–gas transition through have higher latent heat of phase transition but their large volume changes on phase transition. The system is complex and impractical due to large changes in volume. Liquid–gas have comparatively higher latent heat than Solid–liquid but Solid–liquid transitions is attractive for use in thermal energy storage systems due to change in volume is small. Special volume design of the containers to wholes PCM is required due to the volume changes of the PCMs on melting. Any latent heat energy storage system therefore, possess at least following three components:

1. A suitable PCM with its melting point in the desired temperature range,
2. A suitable heat exchange surface, and
3. A suitable container compatible with the PCM.

2.4 Thermo Chemical Energy Storage

Thermo chemical systems depend on the energy absorbed and released in breaking and reforming molecular bonds in a completely reversible chemical reaction [2]. In this case, the heat stored depends on the amount of storage material, the endothermic heat of reaction, and the extent of conversion.

$$Q = a_r m \Delta h_r \quad (4)$$

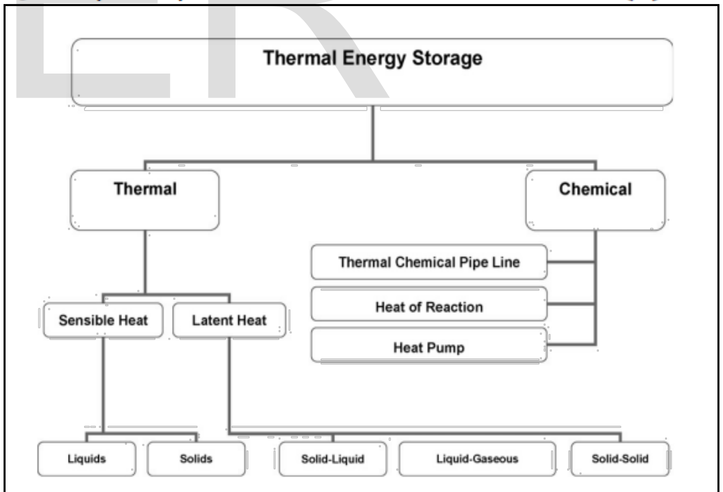

Fig. 1 Different types of thermal storage of solar energy. [2].

3. Latent Heat Storage Material

Phase change materials (PCM) are ‘‘Latent’’ heat storage Materials. When the material changes in state from solid to liquid or liquid to solid, the thermal energy transfer take place. PCM absorbs and release heat at a nearly constant temperature while sensible storage materials absorbs heat leading to temperature rising. PCMs store more heat per unit volume than sensible storage materials. There are large numbers of PCMs melt in any required range with a heat of fusion.

4. Classification of PCMs

A large number of phase change materials (organic, inorganic and eutectic) are available in any required temperature range [2]. A classification of PCMs is given in Figure 2.Depending on the applications; the PCMs should first be selected based on their melting temperature. Majority of phase change materials does not satisfy the criteria required for an adequate storage media as discussed earlier so the poor physical property of the available materials are improved by suitable system design. For example metallic fins can be used to increase the thermal conductivity of PCMs [3].

For their very different thermal and chemical behavior, the properties of each subgroup which affects the design of latent heat thermal energy storage systems using PCMs of that subgroup are discussed in detail below.

4.1 Organic Phase Change Materials

Organic materials are further described as paraffin and non-paraffin. Organic materials include congruent melting means melt and freeze repeatedly without phase segregation and consequent degradation of their latent heat of fusion, self-nucleation means they crystallize with little or no super cooling and usually non-corrosiveness.

4.1.1 Paraffins

The normal Paraffins of type $C_nH_{2n+2}$are a family of saturated hydrocarbons with very similar properties. Paraffins between C 5 and C 15 are liquids, and the rest are waxy solids. Paraffin wax is the most-used commercial organic heat storage PCM. It consists of mainly straight chain hydrocarbons that have melting temperatures ranging from 23 to 67 ° C. Commercial-grade paraffin wax is obtained from petroleum distillation and is not a pure substance, but a combination of different hydrocarbons. Commercial paraffin waxes are inexpensive with moderate thermal storage densities and a wide range of melting temperatures so Paraffin qualifies as heat of fusion storage materials .Both the melting point and latent heat of fusion increase with chain length.Table 1a lists thermal properties of some technical grade paraffins, which are essentially, paraffin mixtures and are not completely refined oil. Only technical grade paraffins can be used as PCM where pure paraffin waxes are very expensive.

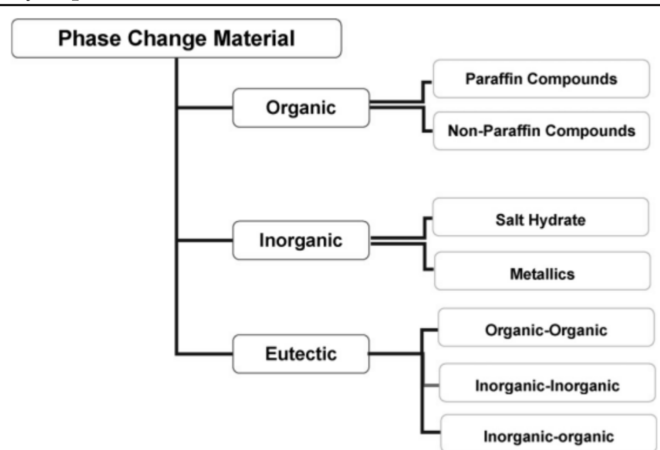

Fig. 2 Classification of PCMs [2].

The advantages of paraffin's are chemically stable with no phase segregation, high heats of fusion, freeze without much super cooling, safe and non-reactive, compatibility with conventional material of construction and recyclable. However, the disadvantages of paraffin's are low thermal conductivity, on compatible with the plastic container, have high volume change between the solid and liquid stages and volumetric latent heat storage capacity is low.

Some selected paraffin's are shown in Table1b along-with their melting point, latent heat of fusion and groups. PCMs are categorized as: (i) group I, most promising; (ii) group II, promising; and (iii) group III, less promising [2, 3].

Table 1a Physical properties of some paraffin'

paraffin'	Freezing point/rang (°c)	Heat of fusion (kJ/kg)	Group
6106	42–44	189	I
P116	45–48	210	I
5838	48–50	189	I
6035	58–60	189	I
6403	62–64	189	I
6499	66–68	189	I

Table 1b Melting point and latent heat of fusion: paraffins

No. of carbon atoms	Melting point	Latent heat of fusion (kJ/kg)	GrouP
14	5.5	228	I
15	10	205	II
16	16.7	237.1	I
17	21.7	213	II
18	28.0	244	I
19	32.0	222	II
20	36.7	246	I
21	40.2	200	II
22	44.0	249	II
23	47.5	232	II
24	50.6	255	II
25	49.4	238	II
26	56.3	256	II
27	58.8	236	II
28	61.6	253	II
29	63.4	240	II
30	65.4	251	II
31	68.0	242	II
32	69.5	170	II
33	73.9	268	II
34	73.9	269	II

"Group I, most promising; group II, promising; group III, less promising—;insufficient data."

4.1.2 Non-Paraffins

The largest category of candidate materials for latent heat storage considered is non-paraffins. Lane Abhat and Buddhi et al. have conducted an extensive survey of organic materials and identified a number of esters, fatty acids, alcohols, and glycols suitable for energy storage. These organic materials are further sub-groups of fatty acids and other non-paraffin organics. The non-paraffin organics are the most numerous of the PCMs, with highly varied properties, unlike the paraffins, which have very similar properties. These materials are flammable and should not be exposed to excessively high temperature, flames or oxidizing agents. Some of the features of these organic materials are as follows: (i) high heat of fusion, (ii) inflammability, (iii) low thermal conductivity, (iv) low flash points, (v) varying level of toxicity, and (vi) instability at high temperatures.

The thermal properties of fatty acids are attractive candidates for latent heat thermal energy storage in space heating applications by Feldman and Shapiro analysis [4]. Fatty acids have high heat of fusion values comparable to that of paraffin's. Fatty acids freeze with no super cooling. The general formula of all the fatty acid is given by CH 3 (CH 2) 2n.COOH and hence, qualifies as good PCMs. the major drawback of fatty acids is their cost, which are 2–2.5 times greater than that of technical grade paraffin's. They are also mild corrosive [2, 3].

4.2 Inorganic Phase Change Materials

Inorganic materials are further classified as salt hydrate and metallic.

4.2.1 Salt Hydrates

Salt hydrates are the most important group of PCMs and the oldest studied for their use in latent heat thermal energy storage. The general formula of Salt hydrates is AB. n H_2O. The solid–liquid transformation of salt hydrates is actually a dehydration of hydration of the salt, although this process resembles melting or freezing thermodynamically. A salt hydrates usually melts to either to a salt hydrate with fewer moles of water, i.e.

$$AB.nH_2O \rightarrow AB.mH_2O + (n-m)H_2O \quad (6)$$

$$AB.nH_2O \rightarrow AB + nH_2O \quad (7)$$

At the melting point the hydrate crystals breakup into anhydrous salt and water, or into a lower hydrate and water. The released water of crystallization is not sufficient to dissolve all the solid phase present leading to incongruent melting of most salt hydrates. The lower hydrate (or anhydrous salt) settles down at the bottom of the container due to density difference.

Advantages of salt hydrates

1-Low cost, easy availability of salt hydrates makes them attractive for heat storage applications.

2- High volumetric latent heat storage capacity

3-High thermal conductivity

4-High heat of fusion and lower volume change than other PCMs.

Disadvantages of salt hydrates

1-Segregation and super cooling of salt hydrates.

2- Nucleating agents are needed and they often become inoperative after repeated cycling.

The reduction in active volume available for heat storage is due to segregation. Segregation is a formation of other hydrates or dehydrated salts that tend to settle out. Another material can be added to the salt hydrate to prevent Segregation where it can hinder the heavier phases to sink to the bottom.

Segregation can be prevented by addition another material to the salt hydrate that can hinder the heavier phases to sink to the bottom. This can be achieved either thickening materials or gelling. Thickening means the addition of a material to the salt hydrate that increases the viscosity and hereby holds the salt hydrate together. Gelling means adding a cross-linked material (e.g., polymer) to the salt to create a three dimensional network that holds the salt hydrate together [5]. Abhat reported that a decrease in heat of fusion of over 73% in $Na_2SO_4.10H_2O$ after 1000 melt/freeze cycles. Salt hydrates show supercooling because they do not start to crystallize at the freezing point of other PCMs [3]. This can be avoided using suitable nucleating materials to start crystal growth in the storage media.

4.2.2. Metallics

Metallics are described as the low melting metals and metal eutectics. Due to weight penalties of these metallics, they have not yet been seriously considered for PCM. However, when volume is a consideration, they are likely candidates because of the high heat of fusion per unit volume. They have high thermal conductivities, so fillers with added weight penalties are not required. The use of metallic poses a number of unusual engineering problems. A major difference between the metallics and other PCMs is their high thermal conductivity.

Some of the features of these materials are as follows: (i) low heat of fusion per unit weight (ii) high heat of fusion per unit volume, (iii) high thermal conductivity, (iv) low specific heat and (v) relatively low vapor pressure [2].

4.3 Eutectics

A eutectic is a minimum melting composition of two or more components, each of which melts and freezes congruently, forming a mixture of the component crystals during crystallization. Eutectics nearly always melt and freeze without segregation because they freeze to an intimate mixture of crystals, leaving little opportunity for the components to separate. On melting, both components liquefy simultaneously, again with separation unlikely.

The advantages of eutectic are that have sharp melting point similar to pure substance and volumetric storage density is slightly above organic compounds. The disadvantage of eutectic is that limited data is obtained about the thermo-physical properties as the use of these materials are very new to thermal storage application. Some segregation PCM compositions have sometimes been incorrectly called eutectics, since they are minimum melting. Because of the components undergoes a peritectic reaction during phase transition, however, they should more properly be termed peritectics [2].

5. Measurement Techniques of Thermo-Physical Properties

There are four types of measurement techniques used for latent heat of fusion and melting temperature of PCMs: (1) Drop Calorimeter (DC) (2) Differential Thermal Analysis (DTA) and (3) Differential Scanning Calorimeter (DSC). (4) T-history method [2, 3] [5, 6].

6. Phase Change Material (PCM) Containers

The PCM is selected based on the temperature range of application. Then the next most important factors to consider are: (i) The geometry of the PCM container and (ii) The thermal and geometric parameters of the container required for a given amount of PCM.

The shape and size of phase change material (PCM) container have to correspond to the melting time of the PCM and the daily insulation at a given location to ensure long-term thermal performance of any PCM system, if the source of energy is a solar. The rectangular and cylindrical containers were used in many papers dealing with LHTES. The shell and tube system is the most intensely analyzed as LHTES unit due to the most engineering systems employ cylindrical pipes and also heat loss from the shell and tube system is minimal. Figure 3. gives the schematics of the cylindrical and rectangular containers [7].

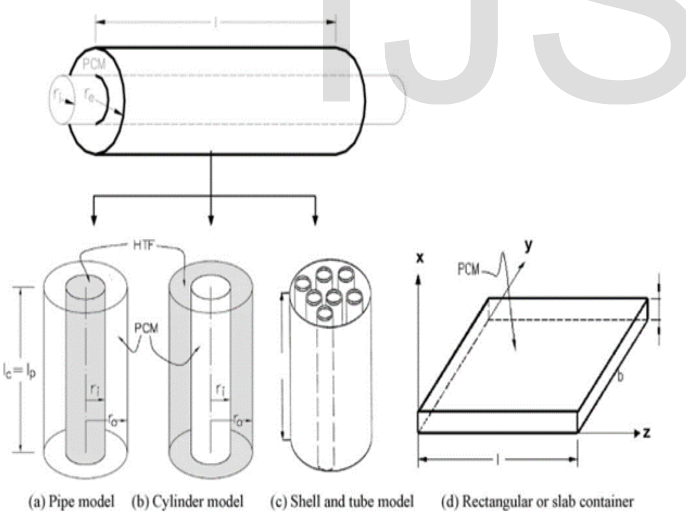

Fig. 3. Classification of commonly used PCM containers in terms of the geometry and configuration [7]

6.1 Configurations of Cylindrical PCM Containers

There are three modes of cylindrical PCM container configurations. The first is the pipe model where the PCM fills the shell and the heat transfer fluid flows through a single tube (Figure 3a). In the second model (cylinder model) the PCM fills the tube and the HTF flows parallel to the tube (Figure 3b). Esen et al studied the two models theoretically and recommended the pipe model because it recorded a shorter melt time and it has a lower heat loss rate to the environment because most heat supplied from the center ends up heating the PCM .The study of two models was by comparing the effects of various thermal and geometric parameters; cylinder radii, total PCM volume, mass flow rates and inlet temperatures of HTF on the storage time. The third cylinder model is the shell and tube system (Figure 3c) commonly used to improve heat transfer in PCMs.

Agyenim et al. conducted an experimental energy storage system to compare horizontal shell and tube heat exchanger (4 tubes) and a pipe model incorporating a medium temperature phase change material (erythritol) with a melting point of 117.7 °C. Isothermal contour plots and temperature time curves were used to analyze the thermal characteristics in the systems. Temperature gradients along the three directions of the two systems; axial, radial and angular directions were also analyzed and compared. The effect of multiple convective heat transfer in the shell and tube system was found to be dominated compared to conductive heat transfer in the pipe model. In the axial direction for both the pipe and shell and tube systems, the temperature gradients recorded during the change of phase were reported to be 2.5% and 3.5% that of the radial direction respectively, indicating essentially a two-dimensional heat transfer in both systems. In the shell and tube system, the completed melt time is 5 h compared to more than 8 h for the pipe model due to the natural convection through the formation of multiple convective cells in the shell and tube system significantly altered the shape of the solid liquid interface fluid flow. Many authors recommended that using the shell and tube configuration followed by the pipe model with the PCM at the shell side and the heat transfer fluid flowing through the center due to its superior performance [7].

6.2. Cunter-Current and Parallel HTF Flow Directions

In a cylindrical container assembly, there are two modes of flow direction of the heat transfer fluid during charging and discharging of the PCM energy (1) parallel flow where the hot and cold fluid are introduced into the tube from the same end (2) counter-current flow where the hot and cold fluid are introduced from the opposite ends of the heat transfer tube during charging and discharging respectively. Gong and Mujumdar conducted the numerical simulations to investigate the effect of the parallel and counter-current flow modes.It was showed that parallel flow increases the energy charge/discharge rate by 5% more than counter-current flow, this was due to higher temperature difference at the fluid inlet if hot and cold fluid enters from the same end. In addition, super cooling of the PCM did not occur in the fluid inlet region and heat transfer between the heat transfer fluid and the PCM did not deteriorate. On the other hand, counter-current flow for the charge/discharge processes produced significant super-cooling of the PCM in the inlet region of the cold fluid [7].

7. Thermal Energy Storage Systems Or Applications of PCMs

Different researchers used PCMs in a lot of applications such as Solar water-heating systems, space heating, Solar air heating systems, Solar cookers, greenhouse heating, space cooling, waste heat recovery system, Buildings(PCM Trombe wall - PCM wallboards - PCM shutter - Under-floor heating systems -Ceiling boards), Ice storage, Solar power plants, Spacecraft thermal systems, Thermal comfort in vehicles, Cooling of engines (electric and combustion) ,Food agroindustry, wine, milk products (absorbing peaks in demand), greenhouses) ,Thermal protection of food: transport, hotel trade, ice-cream, etc. , thermal management of portable electronic devices ,Medical applications: transport of blood, operating tables, hot–cold therapies, Cooling: use of off-peak rates and reduction of installed power, ice bank , pre-heating of evaporator and pressure regulator of a gaseous sequential injection system and Safety: temperature maintenance in rooms with computers or electrical appliances [3, 4] [8-16].

Conclusion

The paper mainly focus on phase change material (PCM) based on thermal energy storage system. Various types of phase change materials (organic, inorganic and eutectic) are available in a wide range of applied temperature. Thermal energy storage is very important in many engineering applications such solar water-heating systems, space heating, solar air heating systems, solar cookers, greenhouse heating, space cooling, waste heat recovery system, and buildings.

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