Review of Phase Change Materials For Thermal Energy Storage Applications

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Abstract:

Energy storage plays important role in conserving available energy and improving its utilization i.e. stabilizing demand side energy. There is fluctuation in supply side. This paper reviews various Phase Change Materials (PCM) in solar thermal energy storage systems for various types' viz. sensible heat storage, latent heat storage and thermo-chemical storage etc.

The details of various Phase Change Materials, their properties and characteristics are studied and analyzed. In sensible heat storage (SHS), thermal energy is stored by raising the temperature of a solid or liquid. SHS system utilizes the heat capacity and the change in temperature of the material during the process of charging and discharging. Latent heat storage (LHS) is based on the heat absorption or release when a storage material undergoes a phase change from solid to liquid or liquid to gas or vice versa. Molten salt is used in solar power systems because it is liquid at atmosphere pressure, it provides an efficient, low-cost medium & stores thermal energy, and its operating temperatures are compatible with today's high-pressure and high-temperature steam turbines. The molten salt is a mixture of 60 percent sodium nitrate and 40 percent potassium nitrate, commonly called saltpeter. Properties such as Thermal properties, Physical properties, and Chemical properties are important for design of Thermal Energy Storage using PCM.

This paper further revels application of PCM in Concentrating Solar Power using HTF media operating in the range of 290°C to 400°C.System design and sizing of Thermal Energy Storage using PCM is an advance technology and is under research for its use in high temperature applications.

Keywords:

Phase Change Materials (PCM), Properties of PCMs, Molten Salt, Sizing of Thermal Energy Storage

Introduction

Solar energy is available only during the day, and hence, its application requires an efficient thermal energy storage so that the excess heat collected during sunshine hours may be stored for later use during the night. Similar problems arise in heat recovery systems where the waste heat availability and utilization periods are different, requiring some thermal energy storage. Also, electrical energy consumption varies significantly during the day and night, especially in extremely cold and hot climate countries where the major part of the variation is due to domestic space heating and air conditioning. Such variation leads to an off peak period, usually after midnight until early morning. The successful application of load shifting and solar energy depends to a large extent on the method of energy storage used.

The most commonly used method of thermal energy storage is the **sensible heat** method. In solar heating systems, water is still used for heat storage in liquid based systems, while a rock bed is used for air based systems. In the application of load leveling, heat is usually stored in a refractory bricks storage heater, known as a night storage heater. These units are capable of providing space heating during the day from the stored heat during the night, however, they are heavy and bulky in size.

The **latent heat** method of storage has attracted a large number of applications. This method of heat energy storage provides much higher energy storage density with a smaller temperature swing when compared with the sensible heat storage method. However, practical difficulties usually arise in applying the latent heat method due to the low thermal conductivity, density change, stability of properties under extended cycling and sometimes phase segregation and subcooling of the phase change materials.

Classification of PCMs

A large number of phase change materials (organic, inorganic and eutectic) are available in any required temperature range. A classification of PCMs is given as organic, inorganic and eutectic PCMs. There are a large number of organic and inorganic chemical materials, which can be identified as PCM from the point of view melting temperature and latent heat of fusion. As no single material can have all the required properties for an ideal thermal-storage media, one has to use the available materials to match system designs.

Organic phase change materials

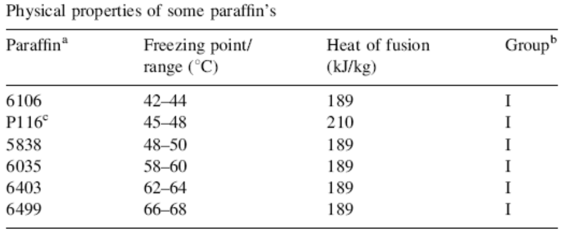
Organic materials are further described as paraffin and nonparaffins.

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 supercooling and usually non-corrosiveness.

Paraffins

Paraffin wax consists of a mixture of mostly straight chain n alkanes CH3–(CH2)–CH3. The crystallization of the (CH3)- chain release a large amount of latent heat. Both the melting point and latent heat of fusion increase with chain length. Paraffin qualifies as heat of fusion storage materials due to their availability in a large temperature range. Due to cost consideration, however, only technical grade paraffins may be used as PCMs in latent heat storage systems

Paraffin is safe, reliable, predictable, less expensive and non-corrosive. They are chemically inert , show little volume changes on melting and have low vapor pressure in the melt form. For these properties of the paraffins, system-using paraffins usually have very long freeze–melt cycle.



Physical properties of some paraffin's

Paraffin[a]	Freezing point/ range (°C)	Heat of fusion (kJ/kg)	Group[b]
6106	42–44	189	I
P116[c]	45–48	210	I
5838	48–50	189	I
6035	58–60	189	I
6403	62–64	189	I
6499	66–68	189	I

Non-paraffins

The non-paraffin organic are the most numerous of the phase change materials with highly varied properties. Each of these materials will have its own properties unlike the paraffin's, which have very similar properties. This is the largest category of candidate's materials for phase change storage. These organic materials are further subgroups as fatty acids and other non-paraffin organic. 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.

Fatty acids have high heat of fusion values comparable to that of paraffin's. Fatty acids also show reproducible melting and freezing behavior and freeze with no supercooling

The general formula describing all the fatty acid is given by CH3(CH2)2n_COOH and hence, qualify as good PCMs. Their major drawback, however, is their cost, which are 2–2.5 times greater than that of technical grade paraffin's. They are also mild corrosive.

Inorganic phase change materials

Inorganic materials are further classified as salt hydrate and metallics. These phase change materials do not supercool appreciably and their heats of fusion do not degrade with cycling

Salt hydrates

Salt hydrates may be regarded as alloys of inorganic salts and water forming a typical crystalline solid of general formula AB.nH2O. 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.

$$AB . nH2O \rightarrow AB. mH_2O + (n - m)H_2O$$

or to its anhydrous form

$$AB . nH2O \rightarrow AB + nH_2O$$

At the melting point the hydrate crystals breakup into anhydrous salt and water, or into a lower hydrate and water. One problem with most salt hydrates is that of incongruent melting caused by the fact that the released water of crystallization is not sufficient to dissolve all the solid phase present. Due to density difference, the lower hydrate (or anhydrous salt) settles down at the bottom of the container. Most salt hydrates also have poor nucleating properties resulting in supercooling of the liquid before crystallization beings. One solution to this problem is to add a nucleating agent.

Salt hydrates are the most important group of PCMs, which have been extensively studied for their use in latent heat thermal energy storage systems. The most attractive properties of salt hydrates are: (i) high latent heat of fusion per unit volume, (ii) relatively high thermal conductivity (almost double of the paraffin's), and (iii) small volume changes on melting. They are not very corrosive, compatible with plastics and only slightly toxic. Many salt hydrates are sufficiently inexpensive for the use in storage.

Three types of the behavior of the melted salts can be identified: congruent, incongruent and semi-congruent melting.

(i) Congruent melting occurs when the anhydrous salt is completely soluble in its water of hydration at the melting temperature.

(ii) Incongruent melting occurs when the salt is not entirely soluble in its water of hydration at the melting point.
(iii) Semi-congruent melting the liquid and solid phases in equilibrium during a phase transition is of different melting composition because of conversion of the hydrate to a lower-hydrated material through loss of water.

The major problem in using salt hydrates, as PCMs is the most of them, which are judged suitable for use in thermal storage, melts incongruently. As n moles of water of hydration are not sufficient to dissolves one mole of salt, the resulting solution is supersaturated at the melting temperature. The solid salt, due to its higher density, settles down at the bottom of the container and is unavailable for recombination with water during the reverse process of freezing. This result in an irreversible melting–freezing of the salt hydrate goes on decreasing with each charge–discharge cycle.

Another important problem common to salt hydrates is that of supercooling. At the fusion temperature, the rate of nucleation is generally very low. To achieve a reasonable rate of nucleation, the solution has to be supercooled and hence energy instead of being discharged at fusion temperature is discharged at much lower temperature.

Other problem faced with salt hydrates is the spontaneous of salt hydrates with lower number of water moles during the discharge process. Adding chemicals can prevent the nucleation of lower salt hydrates, which preferentially increases the solubility of lower salt hydrates over the original salt hydrates with higher number of water moles.

The problem of incongruent melting can be tackled by one of the following means: (i) by mechanical stirring (ii) by encapsulating the PCM to reduce separation (iii) by adding of the thickening agents which prevent setting of the solid salts by holding it in suspension (iv) by use of excess of water so that melted crystals do not produce supersaturated solution , (v) by modifying the chemical composition of the system and making incongruent material congruent

How do phase-change materials work in solar heat storage?

PCM's are chemical substances that undergo a solid-liquid transition at temperatures within the desired range for heating purposes. During the transition process, the material absorbs energy as it goes from a solid to a liquid and releases energy as it goes back to a solid.

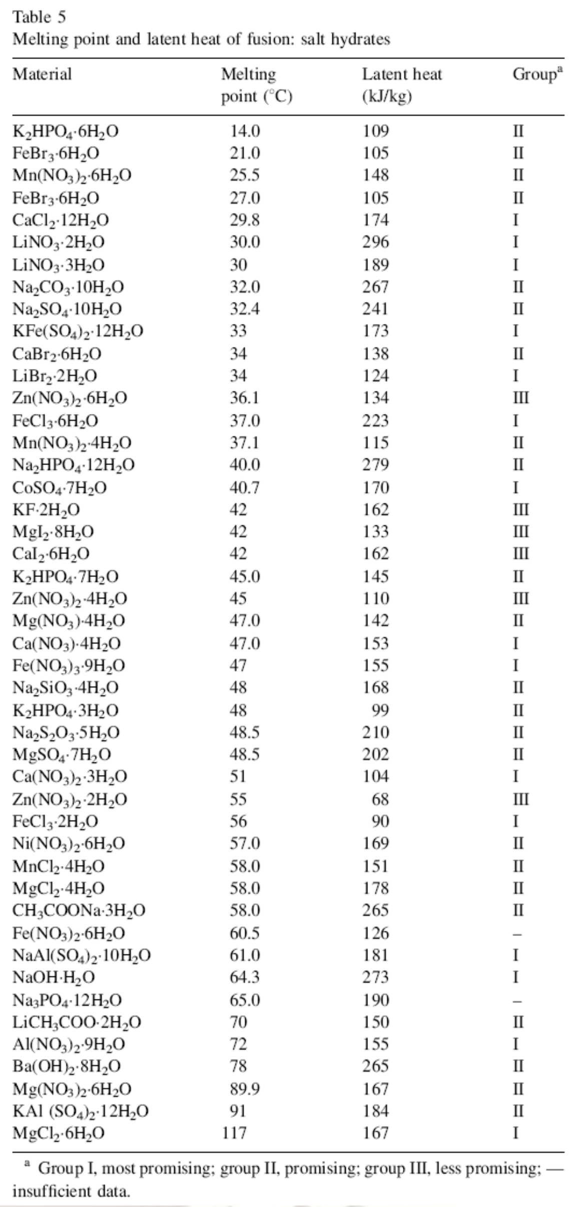


Table 5
Melting point and latent heat of fusion: salt hydrates

Material	Melting point (°C)	Latent heat (kJ/kg)	Group[a]
$K_2HPO_4 \cdot 6H_2O$	14.0	109	II
$FeBr_3 \cdot 6H_2O$	21.0	105	II
$Mn(NO_3)_2 \cdot 6H_2O$	25.5	148	II
$FeBr_3 \cdot 6H_2O$	27.0	105	II
$CaCl_2 \cdot 12H_2O$	29.8	174	I
$LiNO_3 \cdot 2H_2O$	30.0	296	I
$LiNO_3 \cdot 3H_2O$	30	189	I
$Na_2CO_3 \cdot 10H_2O$	32.0	267	II
$Na_2SO_4 \cdot 10H_2O$	32.4	241	II
$KFe(SO_4)_2 \cdot 12H_2O$	33	173	I
$CaBr_2 \cdot 6H_2O$	34	138	II
$LiBr_2 \cdot 2H_2O$	34	124	I
$Zn(NO_3)_2 \cdot 6H_2O$	36.1	134	III
$FeCl_3 \cdot 6H_2O$	37.0	223	I
$Mn(NO_3)_2 \cdot 4H_2O$	37.1	115	II
$Na_2HPO_4 \cdot 12H_2O$	40.0	279	II
$CoSO_4 \cdot 7H_2O$	40.7	170	I
$KF \cdot 2H_2O$	42	162	III
$MgI_2 \cdot 8H_2O$	42	133	III
$CaI_2 \cdot 6H_2O$	42	162	III
$K_2HPO_4 \cdot 7H_2O$	45.0	145	II
$Zn(NO_3)_2 \cdot 4H_2O$	45	110	III
$Mg(NO_3) \cdot 4H_2O$	47.0	142	II
$Ca(NO_3) \cdot 4H_2O$	47.0	153	I
$Fe(NO_3)_3 \cdot 9H_2O$	47	155	I
$Na_2SiO_3 \cdot 4H_2O$	48	168	II
$K_2HPO_4 \cdot 3H_2O$	48	99	II
$Na_2S_2O_3 \cdot 5H_2O$	48.5	210	II
$MgSO_4 \cdot 7H_2O$	48.5	202	II
$Ca(NO_3)_2 \cdot 3H_2O$	51	104	I
$Zn(NO_3)_2 \cdot 2H_2O$	55	68	III
$FeCl_3 \cdot 2H_2O$	56	90	I
$Ni(NO_3)_2 \cdot 6H_2O$	57.0	169	II
$MnCl_2 \cdot 4H_2O$	58.0	151	II
$MgCl_2 \cdot 4H_2O$	58.0	178	II
$CH_3COONa \cdot 3H_2O$	58.0	265	II
$Fe(NO_3)_2 \cdot 6H_2O$	60.5	126	–
$NaAl(SO_4)_2 \cdot 10H_2O$	61.0	181	I
$NaOH \cdot H_2O$	64.3	273	I
$Na_3PO_4 \cdot 12H_2O$	65.0	190	–
$LiCH_3COO \cdot 2H_2O$	70	150	II
$Al(NO_3)_2 \cdot 9H_2O$	72	155	I
$Ba(OH)_2 \cdot 8H_2O$	78	265	II
$Mg(NO_3)_2 \cdot 6H_2O$	89.9	167	II
$KAl\ (SO_4)_2 \cdot 12H_2O$	91	184	II
$MgCl_2 \cdot 6H_2O$	117	167	I

[a] Group I, most promising; group II, promising; group III, less promising; — insufficient data.

As on date , **Glauber's salt (sodium sulfate decahydrate)** is being sold commercially. Glauber's salt changes phases at 90°F and has a 108-BTU-per-pound "latent heat" (amount of heat absorbed or released during phase change). Because of its high latent heat, Glauber's salt requires less storage volume than either rock or water; that could mean lower storage facility cost and more usable space within the home to offset the material's relatively high cost. PCM's do have some chemical traits that can present problems in heat storage and transfer; but most have been or are being overcome. One is that PCM's tend to overcool as heat is withdrawn. This means that, rather than giving up its latent heat at the phase-change temperature, salt PCM's may remain a liquid until they fall to possibly 15-30°

below that temperature. To combat this super cooling in Glauber's salt, about 3 percent of the chemical, sodium tetraborate decahydrate, is added to induce phase change at the proper temperature.

Another problem with salt PCM's is that of incongruent melting, which occurs when the salt is partially insoluble in the water of crystallization. In the case of Glauber's salt, at its melting temperature, about 15 percent of the sodium sulfate remains in insoluble anhydrous form. Being twice as dense as the saturated solution, the anhydrous settles out and will not recrystallize when heat is withdrawn. To prevent this, a thickening agent is used to keep the hydrous in suspension until it can reform in the crystal structure when heat is removed.

Phase segregation and subcooling problems

The high storage density of salt hydrate materials is difficult to maintain and usually decreases with cycling. This is because most hydrated salts melt congruently with the formation of the lower hydrated salt, making the process irreversible and leading to the continuous decline in their storage efficiency. Subcooling is another serious problem associated with all hydrated salts. In an effort to overcome these problems, a number of investigators have used hydrated salts in direct contact heat transfer between an immiscible heat transfer fluid and the hydrated salt solution, as will be described later. The agitation caused by the heat transfer fluid has minimized the subcooling and prevented phase segregation. The hydrated salts studied were $CaCl_2 .6H_2O$, $Na_2SO_4 . 10H_2O$, $Na_2HPO_4 . 12H_2O$, $NaCO_3 .10H_2O$, and $Na_2 S_2O_4 .5H_2O$.

Stability of thermal properties under extended cycling

The most important criteria that have limited widespread use of latent heat stores are the useful life of PCMs–container systems and the number of cycles they can withstand without any degradation in their properties. Insufficient long term stability of the storage materials is due to two factors: poor stability of the materials properties and/or corrosion between the PCM and the container.

The development of PCM containers must be directed towards demonstration of physical and thermal stability, as the PCMs must be able to undergo repetitive cycles of heating and cooling. The purpose of these thermal cycling tests is to determine whether these thermal exposures will result in migration of the PCM or may affect the thermal properties of the PCM. NaCl is used to improve the stability of $CaCl_2. 6H_2O$, containing slightly more water than the stoichiometric composition.

Encapsulation of phase change materials

There are many advantages of microencapsulated PCMs, such as increasing heat transfer area, reducing PCMs reactivity towards the outside environment and controlling the changes in the storage material volume as phase change occurs. Microencapsulation of $CaCl_2 .6H_2O$ in polyester resin was particularly successful, and the developments of wall and floor panels were studied. Macroencapsulation of $CaCl_2 .6H_2O$ in plastic film containers appears promising for heating systems using air as the heat transfer medium

Molten salt storage

Molten salt is used in solar power tower systems because it is liquid at atmosphere pressure, it provides an efficient, low-cost medium in which to store thermal energy, its operating temperatures are compatible with today's high-pressure and high-temperature steam turbines, and it is non-flammable and nontoxic. In addition, molten salt is used in the chemical and metals industries as a heat-transport fluid, so experience with molten-salt systems exists in non-solar settings.

The molten salt is a mixture of 60 percent sodium nitrate and 40 percent potassium nitrate, commonly called saltpeter. New studies show that calcium nitrate could be included in the salts mixture to reduce costs and with technical benefits. The salt melts at 220 °C (430 °F) and is kept liquid at 290 °C (550 °F) in an insulated storage tank. The uniqueness of this solar system is in de-coupling the collection of solar energy from producing power, electricity can be generated in periods of inclement weather or even at night using the stored thermal energy in the hot salt tank. Normally tanks are well insulated and can store energy for up to a week. As an example of their size, tanks that provide enough thermal storage to power a 100-megawatt turbine for four hours would be about 9 m (30 ft) tall and 24 m (80 ft) in diameter.

Sodium sulfate decahydrate (Na2SO4.10H2O) is known to decompose peritetically upon heating to 32.4 C to yield anhydrous sodium sulfate and a saturated solution of Na2SO4 in water. Results are presented for an experimental study designed to find out a means for obtaining many of the advantages of the Na2SO4-H2O reaction for thermal energy storage while eliminating the solid state diffusion problem. Three different compositions were considered: 100 wt% Na2SO4.10H2O, 75.7 wt% Na2SO4.10H2O and 24.3 wt% H2O, and 68.2 wt% Na2SO4.10H2O and 31.8

wt% H2O. It is shown that best results can be obtained by using the third mixture as a thermal energy storage material.

Conclusions

Organic and inorganic compounds are the two most common groups of PCMs. Most organic PCMs are non-corrosive and chemically stable, they exhibit little or no subcooling, and are compatible with most building materials and have a high latent heat per unit weight and low vapor pressure. Their disadvantages are low thermal conductivity, high changes in volume on phase change and flammability.

Inorganic compounds have a high latent heat per unit volume and high thermal conductivity and are non-flammable and low in cost in comparison to organic compounds. However, they are corrosive to most metals and suffer from decomposition and subcooling, which can affect their phase change properties. The applications of inorganic PCMs require the use of nucleating and thickening agents to minimize subcooling and phase segregation. R & D efforts are required to discover those agents for commercialization. The applications in which PCMs can be applied are vast, and includes heat and coolness storage in buildings to thermal storage in satellites and protective clothing. A PCM with an easily adjustable melting point would be a necessity as the melting point is the most important criterion for selecting a PCM for passive solar applications. Many more applications are yet to be discovered.

The heat storage applications used as a part of solar water-heating systems, solar air heating systems, solar cooking, solar green house, space heating and cooling application for buildings, off-peak electricity storage systems, waste heat recovery systems etc.

References :

1) H.p.garg and j prakash- Solar energy- fundamentals and applications
2) S.p.sukhatme -Solar energy – principles of thermal collection and storage
3) M.ravikumar, Dr. Pss. Srinivasan- Phase change material as a thermal energy storage material for cooling of building- journal of theoretical and applied information technology
4) Mohammed m. Farid, Amar m. Khudhair, Siddique ali k. Razack,
Said al-hallaj - A review on phase change energy storage: materials and applications- energy conversion and management 45 (2004) 1597–1615
5) Atul sharma ,V.v. Tyagi, C.r. Chen , D. Buddhi - A review on phase change energy storage: materials and applications- renewable and sustainable energy reviews 13 (2009) 318–345
