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Heat storage materials, geometry and applications: A review

Abhay Dinker^a, Madhu Agarwal^{a,*}, G.D. Agarwal^b

^a Department of Chemical Engineering, Malaviya National Institute of Technology, Jaipur, India
^b Department of Mechanical Engineering, Malaviya National Institute of Technology, Jaipur, India

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ABSTRACT

This paper reviews various kinds of heat storage materials, their composites and applications investigated over the last two decades. It was found that sensible heat storage systems are bulkier in size as compared to the latent heat storage systems. Latent heat storage system using phase change materials (PCMs) stores energy at high density in isothermal way. Various geometries of PCM containers used for enhancement of heat transfer area, materials used for the construction of PCM containers and their interaction with heat storage materials are studied. The choice of storage material depends on the desired temperature range, application of thermal storage unit and size of thermal storage system. Low temperature heat storage system uses organic phase change materials while inorganic phase change materials are best suited for high temperature heat storage. Heat transfer within the PCM can be enhanced by preparing composite of high thermal conductivity as well as by altering the geometrical design like addition of fins, use of straight and helical tubes etc. Shell and tube configurations were mostly used for thermal storage systems. Heat transfer enhancement using PCM composite is a promising approach as it reduces cost and bulkiness to the system.

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1. Introduction

Energy storage techniques is one of the major concerns of the present century due to shortage of conventional nonrenewable sources of energy, increased environmental pollution, increased gap between energy supply and demand, and non-uniform distribution of renewable energy sources like solar energy, wind energy, geothermal energy and energy from ocean currents. Energy recovery systems also encountered with the problem of utilization and availability of energy at different time intervals and hence require energy storage systems for uninterrupted power supply [1,2]. Present energy storage systems relies on electrochemical energy in which Li ion batteries have shown their great potential and acquired a large portion of energy storage market as compare to conventional lead acid batteries [3]. The major advantage of using batteries is high energy density storage while the disadvantage is environmental pollution caused during their disposal [4].

Another form of energy storage includes sensible heat storage or latent heat storage. Sensible heat storage system is based on the temperature of the material, its weight, its heat capacity [5] and these systems are bulkier in size require more space. Compare to the sensible energy storage systems latent heat storage systems are attractive in nature due to compact size and high energy density. Latent heat storage systems stores heat as latent heat during change in the phase of material from solid to liquid or liquid to vapor and vice versa [6]. Amount of energy stored by latent heat energy system is more as compared to the sensible energy system as former one not only retain heat as latent heat but also as sensible heat which get absorbed when the temperature of the material rise up to its melting point. The materials used in latent heat storage systems are known as Phase Change Materials (PCMs) which also explains its nature during their application [7]. Depending on the chemical nature these PCMs are categorized as organic and inorganic materials. Selection of material depends on the application and temperature range of heat storage unit. The major disadvantage associated with phase change materials is their poor thermal conductivity hence various modification have been tried to enhance the material properties using composites prepared from phase change materials and materials with high thermal conductivity [8,9].

^{*} Corresponding author. Tel.: +91 0141 2713498 (Office), +91 9413349429 (Mobile). E-mail addresses: madhunaresh@gmail.com, magarwal.chem@mnit.ac.in (M. Agarwal).

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Various experimental and numerical works related to heat storage devices were reviewed. These heat storage units were cylindrical shell type with single concentric [10,11] and multiple tubes for HTF flow [12], Rectangular shell with multiple tubes for HTF flow [13], Triplex tube with PCM in between two sided HTF flow [14] etc. Some work also involved addition of longitudinal and axial fins to enhance thermal conductivity by providing more surface area that promotes enhanced heat transfer by conduction [15–17].

This paper reviewed various heat storage materials, geometry and performance of heat storage units. Sensible heat storage units found to be having bulkier size as compared to latent heat storage units. Various kinds of composites with improved thermal properties were investigated for optimum storage of heat. These materials enhanced the amount of heat stored by the system at small volumes. Geometrical designs of different heat storage units were reviewed to find out the suitable design for optimum transfer of heat.

2. Sensible heat storage systems

Heat storage by increasing the temperature of the material known as sensible heat storage. Materials used for an efficient sensible heat storage system should have high specific heat capacity, long term stability in terms of thermal cycling and should be compatible to the container material in which storage takes place [18]. A variety of materials have been used in the past for sensible heat storage systems classified as liquid heat storage materials and solid heat storage materials [19]. A list of different materials used for sensible heat storage along with their properties is presented in Table 1 and these materials include metals like aluminium, copper, lead etc. [20-22]. These materials comprise high thermal conductivity and hence reduce charging and discharging time although they are also having low heat capacity, high density and high cost that make system expensive to use. Some building materials were also studied as sensible heat storage materials and they are used to build temperature controlled building or energy efficient building $\begin{bmatrix} 23-27 \end{bmatrix}$. It is observed that water is a good sensible heat storage media due to its high thermal conductivity and cheap availability [28,29]. However due to its high vapor pressure water as heat storage material requires insulation and pressure withstanding container for operation at high temperature. Heat storage can be achieved either in fresh water using water storage tank or by employing solar pond which is based on the principle of thermal stratification [30]. Solar water tanks usually fabricated with a variety of materials like steel, concrete, aluminum, fiber glass and lined with insulator at the inner side so to avoid the heat loss through the wall. Solar pond provides an efficient and cheap method to store solar energy at low temperature. Some salts used for solar ponds are magnesium chloride and sodium chloride. Thermal stratification can be easily achieved in solar pond using different concentration of salts at the different layers of water with maximum temperature at bottom part of the pond where the sun radiation get absorbed. Solar ponds are also easy to handle in terms of removal of water without disturbing the other layers of the pond [31].

Another liquid used to store sensible heat include molten salts, petroleum based oils, and molten metals. Petroleum based oils have low thermal capacities as compare to that of water but due to low vapor pressure these are some good options as sensible heat storage medium.

Various systems related to sensible heat storage have been used for the study in past few decades and these are listed in Table 2. Metals as sensible heat storage provide high thermal conductivity and stores heat in less time as compared to the nonmetals [5]. Although use of metals as sensible heat storage material enhances cost and weight of the system. Various building materials were also investigated to store sensible heat with the aim to reduce cost by reducing investment in heating and cooling devices in the buildings [32–35]. Sensible heating storage materials with high heat capacity need to be developed in order to reduce system volume. Researchers also tried to combine sensible heat storage systems with latent heat storage system to increase the overall efficiency of heat storage system [36]. Application of sensible heat storage materials need to be studied based on the geographical distribution of solar radiation so as to optimize green energy storage in the field and development of energy storage materials for buildings.

3. Latent heat storage systems

Latent heat storage systems absorb and release heat when a material undergoes phase change from solid to liquid and liquid to vapor and these materials are referred as phase change materials [37]. PCM stores heat 5 to 14 times as compared to sensible heat storage materials at constant temperature [38]. To store sufficient latent heat phase change materials should have high latent heat of fusion, high specific heat, high thermal conductivity and small volume change during phase change, little or no sub-cooling. These materials should be chemically stable after repeating thermal cycles and should be non-poisonous, non-corrosive, non-inflammable and should be available on large scale at lower price [39].

 Table1

 Sensible heat storage materials and their thermal properties at 20 °C.

Material	Thermal capacity (kJ/kg K)	Thermal conductivity (W. m/K)	Density (kg/m ³⁾	Energy density (kJ/m ³⁾	References
Aluminium	0.945	238.4	2700	2551.50	[21]
Copper	0.419	372	8300	3477.70	[20]
Iron	0.465	59.3	7850	3650.25	[22]
Lead	0.131	35.25	11340	1485.54	[22]
Brick	0.840	0.5	1800	1512	[23]
Concrete	0.879	1.279	2200	1933.80	[24]
Granite	0.892	2.9	2750	2453	[26]
Graphite	0.609	155	2200	13339.80	[25]
Limestone	0.741	2.2	2500	1852.50	[27]
Sandstone	0.710	1.8	2200	1562	[27]
Water	4.183	0.609	998.3	4175.88	[27]

Tal	ble	2
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Different sensible heat storage systems.

Geometrical configuration	Materials	Parameters investigated	Findings	References
Cylindrical configuration with embedded charging tubes	Concrete, cast steel, cast iron	Charging time, energy storage rate, charging energy efficiency.	 Charging time was reduced to 35.48% with four fins assembly and to 41.41% with six fins assembly. Increased flow rate of heat transfer fluid reduce charging time in cast iron and cast steel as compare to concrete. 	[5]
Packed bed configuration	Rocks for sensible part and mixture of fluoride salts encapsulated in AISI 316 for latent heat part	1D heat transfer model was formulated for the sensible and latent heat sections of TES considering separate fluid, solid and molten phases.	Outflow temperature was stabilized by using PCM on top with 1.33% of total storage volume is sufficient to accomplish stabilization as compare to 4.4% of total energy stored as latent heat energy.	[40]
Packed bed with spheres of Egyptian clay	Egyptian clay	Bed length, particle diameter and mass flow rate	Optimized parameters was 2.1 m for bed length, 0.019 m for particle diameter and 900 kg/h for mass flow rate.	[41]
Packed pebble bed with oil	Rock and oil	Axial temperature distribution with variable electrical heating was studied. Simulation was performed using Schumann model	Large deviation was found in axial temperature distribution between experimental and modeled values due to unaccounted heat loss. A modified Schumann model was implemented to reduce the gaps.	[33]
Cement composite graphite paste	Graphite and cement	Effect of water/cement ratio and graphite on comprehensive strength, thermal conductivity and volume heat capacity were studied	Increasing graphite with decrease in water content improves thermal properties of composite however it decreases the comprehensive strength of composite material and vice versa.	[35]
Concrete modules	High temperature concrete	Composition of concrete modules with its chemical and physical properties were studied.	This study provides guidelines and listed associated restrictions regarding use of high temperature concrete for thermal storage.	[34]

3.1. Classification of phase change material

Phase change materials on the basis of their chemical composition can be classified as organic and inorganic phase change materials [42]. Organic phase change materials are made of hydrocarbons and include paraffin's, fatty alcohols, fatty acids and waxes. Inorganic phase change materials include molten salts, salt hydrates and metallic. Another class of phase change materials includes eutectic mixtures of organic-inorganic, inorganic-inorganic and organic-organic compounds [19,43].

3.2. Thermal properties of phase change material

Selection of right phase change material for thermal storage application is an important part where range of parameters need to be investigated. These parameters include a desired melting point depending on the type of application, desired latent heat of fusion/ vaporization, thermal conductivity and stability of material towards thermal cycling [44–46]. The important criterion for choosing a phase change material is that its melting point should lie in the range for desired application. Organic phase change materials have low melting temperature range and employed for low temperature thermal energy storage systems. Rauaolut et al. [47] used a low temperature thermal energy storage system consisting of paraffin wax as phase change material to control temperature of room. The storage system depends on thermal gap between night time and daytime outdoor air temperature to refresh indoor air using molten phase of paraffin. Bruno et al. [48] used PCM with melting point 10 °C inside the tubes of thermal storage unit coupled with ice based system and found that about 13.5% energy recovered by the system which was further enhanced by heat transfer optimization. Similarly inorganic phase change materials lie in the high temperature melting point range and used for high temperature thermal storage like in CSP (Concentrated Solar Plant) [49], thermocline storage material [50] etc.

Table 3 represents thermal properties of some organic and inorganic PCM are used in different applications for latent heat storage. Organic compounds like paraffin, fatty acids, and fatty alcohols have low melting point (10°C–60 °C) and used for low temperature domestic thermal storage. Paraffins are straight chain hydrocarbons and possess desirable properties like high heat of fusion, low vapor pressure, chemical inertness, self-nucleation with no phase segregation. The melting point of paraffin's varies with the number of carbon atoms in the chain. Technical grade paraffin's are cheaper as compared to pure paraffin. Fatty acids are good organic phase change material to store thermal energy at low temperature range also they have high heat of fusion with no super cooling comparable to paraffin wax and salt hydrates [37,51,52]. Fatty acids are stable and reliable in terms of their thermal properties [53]. Sari et al. [54] studied the thermal storage performance of palmitic acid in a tube-in-tube type heat exchanger and reported heat storage efficiency of 53.3%. They also observed that inlet fluid temperature and flow rate does not have any significant effect on the melting time of PCM. However, it was found that melting time had been reduced considerably by placing the tube containing PCM in horizontal position rather than a vertical position. Konukulu et al. [55] prepared microcapsules of capric acids with different shell materials for their use as thermal storage materials. They found that microcapsules with UF shell (E:Tween 40) were found to be stable and hence suitable for thermal storage applications.

Eutectic mixtures of organic and inorganic materials is again matter of interest for past research programs to develop mixtures with desirable melting point, high thermal capacity with no or little super cooling effect. Inorganic eutectic mixtures are suitable for high

Table 3				
Phase change	materials used	for latent	heat storage	•

PCMs	Туре	Melting point (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m.K)	References
Paraffin wax $(C_{13}-C_{18})$	Organic	32	251	0.214	[7,52]
Polyglycol E600	Organic	22	127.2	0.189	[56]
Vinyl stearate	Organic	29	122	0.25	[43]
Butyl stearate	Organic	19	140	0.21	[57,58]
1-Dodecanol	Organic	26	200	0.169	[52,59]
n-Octadecane	Organic	28	243.5	0.148	[60]
Palmitic acid	Organic	57.8	185.4	0.162	[54]
Capric acid	Organic	32	152.7	0.153	[61]
Caprylic acid	Organic	16	148	0.149	[55]
Propyl palmitate	Organic	10	186	n.a	[52]
KNO ₃ /NaNO ₃	Inorganic	220	100.7	0.56	[67]
CaCl ₂ .6H ₂ O	Inorganic hydrates	29	187	0.53	[52]
LiNO ₃ /KNO ₃ /NaNO ₃	Inorganic eutectic mixture	121	310	0.52	[62]
a) KNO3-LiNO3 b) KNO3/NaNO3/LiNO3 Etuectic mixtures	Inorganic eutectic mixtures	124	155	0.58	[63,64]
LiNO ₃ /CaNO ₃ With solar salts NaNO ₃ and KNO ₃	Inorganic	130	276	0.56	[65]
KNO ₃ /NaNO ₃ (30%/70%)	Inorganic Non eutectic mixture	260	305	0.54	[51]
Capric acid (65.12%) and lauric acid (34.88%)	Organic eutectic mixture	19.67	126	0.21	[113]
Polymethylmethacrylate (PMMA)/ capric-stearic acid mixture	Organic eutectic mixture	21.37	116.25	0.15	[66]

temperature thermal storage systems like concentrated solar thermal plant (CSP), while organic eutectics are suitable for low temperature thermal storage like maintaining building temperature. Shilei et al. (2006) studied the eutectic mixture of capric acid and lauric acid for its use in building material and found that these phase change wallboards did not show any variation in melting point and latent heat after 360 thermal cycles and therefore can be used for building energy conservation. Various composition of nitrate salts of potassium, sodium, calcium and lithium were tried by researchers to obtained suitable mixture having desired melting point and latent heat for the purpose of thermal storage [62–64,67]. Sari et al. [66] prepared polymethylmethacrylate (PMMA)/capric-stearic acids eutectic mixture (C-SEM) micro/ nanocapsules for latent heat storage using emulsion polymerization technique. With uniform shape these microcapsules had melting temperature of 21.37 °C with latent heat equal to 116.25 kJ/kg can be used as part of building material for temperature control, however, real world applications of these microcapsules are still need to investigate. All the materials (Table 3) need to be investigated both at microscopic and macroscopic level in order to enhance their thermal property so as to make them useful for commercial application.

3.3. Composites of phase change material

Although phase change materials have been used in wide range of applications to trap heat but they have poor thermal conductivity. Combination of phase change materials with materials of high thermal conductivity attracted the interest of the researchers to use them for various applications. Table 4 shows different composites prepared from organic phase change materials. The materials used to enhance the thermal conductivity of PCMs should have high thermal conductivity, resistant to chemical reaction and should be compatible both with phase change material and material of the container.

Thermal conductivity of pure paraffin is 0.216 W/m.K which increases its melting time and increases the charging time of thermal storage system which can be improved further by adding materials of high thermal conductivity to the paraffin wax. Sahan et al. [68] added nanomagnetite/nanoparticles of magnetite with high thermal conductivity 9.1 W/m.K to enhance the thermal conductivity of paraffin by providing metallic surface area for heat transfer and it is a costlier component which also adds weight to the system. TiO₂ nanoparticles (Harikrishnan et al., 2013) were used with paraffin wax as well as stearic acid to enhance their thermal conductivity. Aluminium foam (218 W/m.K) was also used to enhance thermal conductivity of paraffin [69]. Enhanced thermal conductivity was due to conduction through the aluminum foam as compared to the natural convection. Addition of metal foams or their nano forms will enhance the thermal conductivity but they also added weight to the system and increased the cost of the thermal storage system. Composites of fatty acids and their eutectic mixtures were prepared and tested for thermal storage [53]. Zhang et al. [70] prepared a foam stable composite by incorporating ternary eutectic mixture of lauric acid-palmitic acid-stearic acid (55 wt%) in expanded perlite. The composite had low melting point (31.8 °C) and good latent heat (81.5 kJ/kg) and found to be thermally stable even after 1000 thermal cycles and proved to be a potential energy storage material. The application of this composite as building material component still needs to be investigated. Similarly [107] prepared a composite from eutectic mixture of lauric-myristic-stearic acid and expanded graphite (12:1 w/w) with low melting point (29.05 °C) and good latent heat (137 k]/kg) for low temperature storage applications. They found improved thermal conductivity of eutectic mixture due to addition of expanded graphite and the composite was thermally stable even after 1000 thermal cycles. Yang et al. [72] also prepared composite from eutectic mixture of myristic-palmitic-stearic acid and expanded graphite for thermal storage with a melting point of 41.64 °C and latent heat of 153.5 kJ/kg suitable for solar thermal storage application. Some other composites were also prepared from eutectic mixtures of fatty acids and expanded graphite such as composite of capric-myristic-palmitic acid eutectic mixture with expanded graphite (13:1) [53] and composite of palmitic-stearic acid eutectic mixture with expanded graphite (13:1) [73]. Their corresponding melting points were 18.61 °C and 53.89 °C and latent heats were 128.2 k]/kg and 166.27 k]/kg respectively. Zhang et al. [73] prepared composites of palmitic-stearic acid eutectic mixture and carbon nanotubes (with 5 wt% to 8 wt%). Results showed that thermal

Table 4Composites of organic phase change materials.

Composite	Thermal conductivity (W/m.K)	Observation	Reference
Paraffin wax (80% wt.) with nano magnetite (20% wt.)	0.40	Addition of 20% nanomagnetite enhanced the thermal conductivity of paraffin by 67%. Use of 10% nanomagnetite increased the cost of	[68]
1 Liquid paraffin/aluminium foam 2 Solid paraffin/aluminum foam	1 46.04 2 46.12	composite by 20%. Thermal conductivity of PCM composite increased up to 218 times more as compared to the pure	[69]
Paraffin (80% wt.)/graphite (20% wt.in form of foam, fibers and fins)	0.972	Heat flow much rapidly in porous graphite foam as compared to fin and fiber configuration. More temperature was enhanced using fin configuration	[74]
 Paraffin (80% wt.)/waste graphite (20% wt.) Paraffin (80% wt.)/SFG75 (Timrex powder) (20% wt.) 	1 0.428 2 0.906	as compared to foam and fibers for the same time. 91% enhancement in thermal conductivity of paraffin was observed with waste graphite as compared to 300% enhancement by fresh graphite	[75]
1Paraffin (90% wt.)/expanded graphite (10% wt.) 2 Paraffin (90% wt.)/graphite (10% wt.)	1 0.938 2 0.561	Expanded graphite enhanced thermal conductivity of paraffin by 300% while graphite enhanced the thermal conductivity by 150% as compared to pure paraffin	[76]
Paraffin with expanded graphite (2% wt., 4% wt., 7% wt. and 10% wt.)	0.29, 0.51, 0.68, 0.81 respectively	Thermal conductivity of paraffin increased with increase in graphite content with no leakage up to 10% wt. of graphite.	[77]
Paraffin with TiO ₂ (1%–4% wt.)	0.7	With increase in TiO_2 loading phase change temperature increases with decrease in latent heat capacity. Thermal conductivity of composite	[78]
Eutectic mixture of lauric-palmitic-stearic acid/perlite	0.44	increases with increase in TiO_2 loading upto 3%. Composite was found to be thermally stable after 1000 cycles and well suited as building material for temporature control	[73]
Eutectic mixture of lauric-myristic-stearic acid/expanded graphite (12:1 w/w) composite	-	Addition of expanded graphite enhanced the thermal conductivity of lauric-stearic-myristic acid eutectic mixture. Thermal stability results showed that the mixture was stable after 1000 thermal cycles	[71]
Eutectic mixture of myristic-palmitic-stearic acid/expanded graphite (13:1 w/w) composite	-	Results showed that myristic-palmitic-stearic acid has proper phase change temperature, high latent heat and good thermal conductivity. Prepared composite was also found to be thermally stable	[72]
Eutectic mixture of capric-myristic-palmitic acid/expanded graphite (13:1 w/w)	3.67	Results showed the composite achieved a good thermal conductivity after addition of expanded graphite which enhanced the energy storage and release rate. Also composite was found to be thermally stable after large number of repeating thermal cycles	[79]
Eutectic mixture of palmitic acid —stearic acid/expanded graphite (13 w/w)	2.51	Thermal conductivity of the composite rose significantly which enhanced the heat storage and release rates. Composite was thermally stable and	[70]
Eutectic mixure of lauric-palmitic-stearic acid/Carbon nanotubes (CNTs, 5%—8% w/w)	0.316-0.341	suitable for latent heat storage. Thermal conductivity of the system enhanced with the mass percentage of the added carbon nanotubes. Addition of CNTs increased the heat transfer rate while decreased the amount of heat storage	[80]
Stearic acid with ${\rm TiO_2}$ nano-fluid (0.3% wt.) loading	0.3	Thermal conductivity of the system increases with increase in the TiO_2 percentage with optimum value at 0.3% wt. after which reduction in latent heat was observed	[114]
Stearic acid and silica fumes	_	Form stable composite without leakage of stearic	[81]
Stearic acid with polymethylmethacrylate	_	PMMA support stearic acid which enhanced heat	[81]
 a) Stearic acid with expanded graphite (90% wt.:10% wt.) b) Stearic acid with carbon fiber Both tested for different weight percentage (90% wt.: 10% 	1. 1.1 2. 0.9	Thermal conductivities of PCM increases linearly with increase in weight percentage of graphite. With decrease in latent heat of the composite.	[82]
wt.) Eutectic mixture of lauric acid-stearic acid (7:3 by weight)/ expanded perlite	_	Melting temperature and latent heat hardly varies after 1000 thermal cycle. Expanded perlite provides a good material for support to PCM to prepare an ideal material for thermal storage application	[83]

(continued on next page)

Table 4	(continued)
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Composite	Thermal conductivity (W/m.K)	Observation	Reference
Palmitic acid (80% wt.)/expanded graphite (20% wt.)	0.60	Thermal conductivity of composite is 2.5 times more than thermal conductivity of pure PA.	[109]
 Capric acid (60% wt.)/hallosyte nanotube (40% wt.) Capric acid (60%)/hallosyte nanotube (35% wt.)/ graphite (5% wt.) 	1. 0.479 2. 0.758	Capric acid/hallosyte nanotube composite was formed with 60% of capric acid without leakage. Graphite was used as additive to enhance the thermal conductivity of the composite	[84]
Eutectic mixture of myristic acid/palmitic acid (70% wt.:30% wt.) with 5% wt. sodium myristate.	0.242	Addition of surfactant enhanced the thermal conductivity of fatty acids with increased latent heat of fusion	[85]
Plamitic acid (92% wt.)/graphene nanoplates (8% wt.)	2.11	Graphene nanoparticle s provide more surface for the heat transfer and hence provide 8 times more thermal conductivity then pure palmitate.	[86]
Ternary eutectic mixture of lauric acid/myristic acid/ palmitic acid (55.24% wt.:29.74% wt.:15.02% wt.) with expanded graphite, ratio of ternary mixture to EG is (18:1)	1.67	Ternary mixture of fatty acids stores without leakage at mass ration of (18:1) with EG and distributed uniformly in the porous structure of expanded graphite.	[87]
Capric-myristic acid (50% wt.)/expanded perlite composite (40% wt.)/expanded graphite (10% wt.)	0.076	CA—MA eutectic mixture (0.048 W/m.K) absorbed in the porous structure of perlite and enhanced the thermal conductivity of composite by 60%.	[88]

conductivities of composite PCMs increased by 20.2% (for 5 wt%), 26.2% (for 6 wt%), 26.2% (for 7 wt%) and 29.7% (for 8 wt%) respectively with the addition of carbon nanotubes. It was observed that thermal release rate of composite had increased with addition of carbon nanotubes but heat storage capacity has been decreased. Composites prepared from eutectic mixture of fatty acids can be used as low temperature thermal storage building material. However, low thermal conductivity and high cost of fatty acids make their use limited on commercial scale. Some other low cost materials with high thermal conductivity were also tested with organic compounds to improve thermal properties of material, these materials include carbon materials, graphite [74,75], expanded graphite [76,77], expanded perlite [82], hallosyte nanotube [84], and graphene nano plates [86]. All these are lightweight materials with high thermal conductivity used to improve thermal conductivity without adding weight to the system. Composite not only enhance the thermal property of phase change material but also enhance the thermal storage capacity of the material by providing more surface area for the absorption of phase change material. Composites studied here are not new material in their chemical nature but just the mixture of two different materials. The study of organic composites needs to be done on extensive scale in order to broaden its application area in domestic application and as building wall materials.

As discussed inorganic materials like salts and their eutectic and non-eutectic mixtures were suitable for their high temperature thermal storage. The disadvantages of inorganic PCM were low thermal conductivity, corrosion to the container wall, and high cost in terms of installation and operation which drew the attention of researchers to develop composites of high thermal conductivity. Material used to prepare composite should have high thermal conductivity, resistance to chemical reactions, lighter in weight and it should be compatible with the wall of the container as well as with the PCM. Table 5 listed various composites of inorganic PCM, their eutectic and non-eutectic

Table 5

Composite of inorganic phase change materials.

S. No.	Inorganic composite	Thermal conductivity (W/m.K)	Observation	References
1	KNO ₃ /NaNO ₃ -graphite composite (80% wt./20% wt.)	20	Molten salts also having low conductivity. Thermal conductivity is 20 W/m.K.	[67]
2	Non eutectic mixture KNO3 (30% wt.)/NaNO3 (70%)	0.5	Salt mixture provide wide range of temperature range between 220 and 260 °C for melting and freezing cycle	[51]
3	Lithium carbonate and sodium carbonate/ceramic/ carbon materials (10%)	4.3	Using eutectic mixture of sodium and lithium carbonate on skeleton on magnesium carbonate	[51]
4	Na_2CO_3/MgO composite with added multiwall carbon nanotubes (0.5% wt.)	1.13	Material without added carbon nanotubes showed good thermal stability but poor thermal conductivity.	[89]
5	Cylindrical model of paraffin and porous graphite matrix were studied.	Radial 27.3 Axial 5.3	Increased in graphite content directly proportional to thermal conductivity of composite.	[90]
6	Attapulgite granulate impregnate with the mixture of $\rm MgSO_4$ (20% wt.) and $\rm MgCl_2$ (80% wt.)	-	Hat of absorption increases with increase in the amount of MgCl ₂ due to increase sorption of water in highly concentrated salt solution	[64]
7	LiNO ₃ /KCl (70% wt.)-expanded graphite	15	Presence of EG decrease the latent heat of the composite. Composite with higher density increases the thermal conductivity of the composite.	[91]
8.	LiF-NaF-KF (46.5% wt.,./11.5% wt./42% wt.)	0.92	Salt mixture used to study effect of corrosion on metals. Addition of Ni-201 to alloy reduces the chances of corrosion.	[92]

mixtures for the purpose of high temperature thermal storage. Various composites of inorganic materials were prepared with materials of high thermal conductivity like graphite [67], expanded graphite [90], and multiwall carbon nanotubes [89] etc. and were used to enhanced the thermal conductivity of salts.

4. Geometry of thermal storage systems

For optimum heat storage system selection of PCM and geometry of heat storage unit plays crucial part. Type of PCM for a particular heat storage unit is based on its melting point while geometry of heat storage system drives the heat transfer. Different geometrical designs of thermal storage unit studied are shown in Fig. 1 which includes cylindrical/rectangular heat.

storage unit with HTF (Heat Transfer Fluid) passing through single tube, multiple tubes and triplex tube heat transfer unit with HTF flowing through center and outer of phase change material. In some geometrical arrangements fins were integrated with the tubes to provide more surface area for heat transfer. However addition of fins reduces the amount of PCM in the storage unit and hence reduced overall heat capacity of the system. Material used for PCM container should be well insulated from outside and it should not show any reaction with the phase change material filled inside the container.

Applications, geometry and materials used for heat storage unit are presented in Table 6. Liu et al. [71] studied heat transfer effect in a horizontal acrylic cylindrical container with single copper tube having longitudinal and axial fins as shown in Fig. 1(e) to enhance the heat transfer. It is observed that with increase in heat transfer fluid temperature melting time decreases while there is little effect of variation in flow rate especially when convective heat flow becomes dominant. Study on vertical cylindrical heat storage unit with different arrangement of tubes showed similar effects.

In another study by [93] heat transfer fluid passed through the center and outer part of phase change material (known as triplex tube heat exchanger unit) to reduce charging time of heat storage and found that such assembly led to the heat loss from the outer surface of the unit if it was not properly insulated and therefore not very attractive for heat storage application.

Rectangular shell and tube assembly studied by [94] to consider the effect of fins, fluid flow rate and inlet temperature. Fins were employed to enhance heat transfer so as to reduce the charging time. Results of the study showed that increase in flow rate reduced melting time. Flat plate latent heat storage systems were designed, studied and found that it provides better flexibility in application and insertion of heat enhancement structures [71,95].

5. Corrosion of containers

Containers used for handling phase change materials are operated under different conditions and subjected to variable temperatures which led to the rapid corrosion of the container material if not chosen properly. Ferrer et al. [96] studied the corrosion effect for four different PCMs (one inorganic mixture, one ester, and two fatty acids eutectics) on five different metals (aluminium, copper, carbon steel,



e) Longitudinal and axial fins

Fig. 1. Geometrical design of various thermal storage unit.

Table 6

Different geometrical designs of thermal storage unit.

Geometry and container material	PCM used	Parameters studied	Observations	References
Horizontal cylinder of acrylic plastic with copper pipe containing longitudinal and angular fins	Dodecanoic acid	Effect of inlet temperature and flow rate of HTF, configuration of fins	Both fin arrangement conduction is dominant followed by convection, high inlet temperature reduces melting time, flow rate did not have considerable effect on melting profile of PCM	[97]
Vertical cylindrical of acrylic plastic with two copper pipe connected to longitudinal fins	Dodecanoic acid	Simultaneous charging and discharging rates	Simultaneous heat transfer limited by solid PCM between two pipes, high flow rate of cold HTF allows better heat recovery. Uncertainty in input energy and energy recovery is large	[98]
Double tube heat storage container with outer tube made of steel for PCM storage while inner tube of brass for flow of HTF	Paraffin wax	Effect of increasing inlet temperature and mass flow rate on charging and discharging process of PCM	Heat flow rate increase by 25% and 11% during melting and solidification on increase and decrease of HTF temperature by 2 °C. Increase in 4 °C of temperature of inlet water reduce the melting time by 31%.	[99]
Vertically arranged cylindrical enclosure with vertical pipe along its axis	Paraffin wax	Analysis of PCM melting process with natural convection, duration of melting followed by time dependent numerical simulations.	Numerical simulation validated the features predicted by theory.	[100]
Cylindrical shell and tube type with inner copper tube for HTF flow and outer shell part made of polypropylene	Paraffin wax	Melting profile of paraffin wax were studied at different values of eccentricity i.e. e = 10 mm, 20 mm and 30 mm.	Melting process dominated by conduction followed by convection and more enhanced in upper part of shell. 67% decrease in melting time was observed in case of eccentric geometry = 30 mm than concentric geometry.	[101]
Triplex tube heat exchanger with outer, inner and middle tubes made of copper with PCM filled between the inner tube and middle tube while HTF flows between the middle tube and outer tube	RT82	Heat enhancement techniques were studied using inside outside tube, effect of fin length on enhancement technique were studied.	No considerable effect on melting rate of PCM in both the three enhancement techniques. Complete melting was reduced to 43.3% as compare to TTHX without fin.	[93]
Fin and Tube Heat exchanger with space between the rectangular shell and between the fins filled with PCM	R35	Flow rate, Inlet temperature of HTF and effect of fin pitch on charging and discharging process.	Increasing flow rate from 0.2 L/min to 0.4 L/min at temperature 60 °C showed significant change in PCM melting time while further increase in flow rate reduces it. Melting time also reduces on increasing fin pitch.	[94]
 Studied two systems 1 Shell and tube type with copper tube embedded along with aluminium fins (PCM-HX). 2 Embedded copper tube in the highly conductive graphite- wax composite 	PT43 wax	Comparison of technology to enhance the thermal conductivity of wax was studied, economics of system, charging discharging time, inlet and outlet temperature of HTF were also studied.	PCM HX and Copper tube in composite both performed well in their operations. PCM-HX only occupies 38% of water storage volume as compare to the copper tube based unit. The PCM unit can store 5 times more energy than water in useful range 40°C -52 °C.	[102]
Flat plate latent heat storage. HTF flow in the chamber between the flat carbon steel.	Mobiltherm 603 Thermal conductivity (0.122 W/K)	Temperature gradients, flow rates and insertion of heat transfer structures	Insertion of various heat transfer structures provide phase change discharge time between 2 and 8 h. Flat plate's collector offers wide range of flexibility with HTF, insertion of heat transfer enhancement structure.	[103]
Flat plate latent heat storage unit with flat slabs of phase change material.	Carbonate salts (solar salts), liquid sodium, air, CO ₂ and steam	Comparison between liquid and gaseous HTF, heat transfer characteristics between the slabs, heat transfer rates and liquid fraction profiles were studied	Liquid sodium delivers maximum 99.4% electrical energy to grid relative to the ideal cases. Solar salts achieved 93.6% of electricity delivered while air, CO ₂ and steam delivers 87.9% and 91.3% of electricity delivered.	[71]
Vertical stacks of rectangular cavities filled with PCM	1 Rubitherm RT28HC 2 Micronal DS5001X (Microencapsulated PCM)	Time required for melting and solidification was studied, control temperature value on hot surface of test sample and period of thermal regulation was studied.	Microencapsulated PCM (Micronal DS5001X) accelerated the charging process with no thermal stratification. Control temperature regulation and thermal regulation period both reduced in microencapsulated form. Sub cooling effect cannot be neglected in case of free PCM	[95]
Rectangular container with one wall made up of aluminium alloy. Holes were dig from the aluminium plate side to allow water to pass through the wall as HTF.	Lauric acid	Melt fraction, temporal heat storage, heat transfer characteristics.	Melting initiated by conduction followed by convection. In liquid state of PCM stratification of temperature occurs led to depression of convection.	[104]

stainless steel-304 and -316). Result indicated that aluminium containers showed faster corrosion with inorganic salt mixture and hence caution must be taken while selecting aluminium for PCM containers. Copper showed lower corrosion rate of $6-10 \text{ mg/cm}^2$ yr with the fatty acids formulations and can be used for PCM containers. Stainless steel showed great corrosion resistance of $0-1 \text{ mg/cm}^2$ yr and was the best available material for PCM containers.

Morreno et al. [115] carried out similar study with two metals (i.e. copper and aluminium) and two metal alloy (stainless steel 316 and carbon steel) and selected eleven types of salt mixtures out of which 5 were used for cooling application while 6 PCMs were used for heating applications. The corrosion rate of PCM containers were evaluated after 1 week, 4 week and 12 week. Result of the study showed that thin stainless steel alloy lining should be used with stainless steel and aluminium while later one was suitable only for selected PCM. It was also found that commercial PCM C10 was suitable to encapsulate in stainless steel and aluminium and PCMs used for heating application should be stored in stainless steel container.

In addition to metals and alloys, polymers were also used as container material for phase change material. Oro et al. [105] made comparison between four metals (copper, aluminium, stainless steel and carbon steel) and polymers (polypropylene), High Density Poly Ethylene (HDPE), polyethylene terephthalate and polystyrene. These container materials were tested with four commercial PCM and five developed PCM and observed that carbon steel and copper must be avoided in any situation due to their high reactivity towards corrosion. Aluminium was also not recommended due to the creation of pits on its surface. Stainless steel 316 was well suited material for PCM containers due to its resistivity towards corrosion. Polymer containers did not show any effect on the appearance and weight of the samples. Also there were no pitting, precipitation and bubble formation and hence they are compatible with PCMs.

The studies show that out of the range of selected metals stainless steel was the best available material for PCM container. Polymers are also good choice for phase change materials as they do not show any reactivity with the phase change material as well as they are resistant towards pitting, bubbling and precipitation etc.

6. Conclusion

There are various types of sensible and latent heat systems, their storage materials and their geometrical designs available. Sensible heat storage systems were simple in designs, easy to maintain but bulkier in size. Latent heat systems were found to be more suitable for thermal storage due to their high energy storage density and quasi thermal nature of storage. The low melting point of organic PCMs made them suitable for low temperature applications like domestic water heating, cold storage, as building material etc. While inorganic PCMs due to their high melting point were suitable for high temperature storage application like concentrated solar plant. Low thermal conductivity of both organic and inorganic phase change material had limited their direct use at commercial scale. Composites of organic and inorganic PCMs were prepared with high thermal conductivity materials like graphite, carbon nanotubes, metal oxides, metallic nanoparticles etc. for their large scale application. Composites with expanded graphite and carbon nanotubes were preferred due to high thermal conductivity and low weight. Most of the composites used in thermal storage were mixture of two materials rather than any new substance.

There are different geometrical configurations such as cylindrical shell and tube, rectangular shell and tube, triplex and configurations with longitudinal and axial fins were used with PCMs for thermal storage applications. Addition of fins reduced the melting time of the PCM but it also reduced the amount of PCMs in the system due to space occupancy and hence reduced the overall efficiency of the system. The heat storage units either in cylindrical or rectangular geometry found to be more efficient in their horizontal position as compare to the vertical position. It was due to the presence of large air space above PCM in horizontal position which enhanced conduction heat transfer as compare to the vertical position. Most of the sensible heat storage units used for pre heating of water through solar pond, for pre heating and cooling of air using packed bed configuration, etc. While most of the latent heat storage systems were mostly used for pre heating of water, for pre heating and pre cooling of air, for storage of waste industrial heat and as building materials for temperature control etc. Most of the containers holding PCMs were made of steel and polymers. Corrosion effect of PCMs on container materials has been studied by various researchers. The stainless steel was considered best material for PCMs due to least corrosion at high temperature applications, while containers made up of polymers were good for low temperature applications.

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Further reading

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