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LATENT HEAT STORAGE MATERIALS AND SYSTEMS: A REVIEW

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The use of a latent heat storage system using Phase Change Materials (PCM) is an effective way of storing thermal energy (solar energy, off-peak electricity, industrial waste heat) and has the advantages of high storage density and the isothermal nature of the storage process. It has been demonstrated that, for the development of a latent heat storage system, choice of the PCM plays an important role in addition to heat transfer mechanism. The information on the latent heat storage materials and systems is enormous and published widely in the literatures. In this paper, we make an effort to gather the information from the previous works on PCMs and latent heat storage systems. This review will help to find a suitable PCM for various purposes a suitable heat exchanger with ways to enhance the heat transfer, and it will also help to provide a variety of designs to store the heat using PCMs for different applications, i.e. space heating & cooling, solar cooking, greenhouses, solar water heating and waste heat recovery systems. Measurement techniques of thermophysical properties, studies on thermal cycles for long term stability, corrosion of the PCMs and enhancement of heat transfer in PCM are discussed. New PCM innovations are also included for the awareness of new applications. This paper contains a list of about 250 PCMs and more than 250 references.

Keywords: ***Phase change material, Solar energy, Latent heat storage system, Enhancement of heat transfer, New PCM innovations***

INTRODUCTION

Scientists all over the world are in search of new and renewable energy sources to reduce the CO_2 emissions from the combustion of fossil fuels, particularly in areas where low temperature applications are involved. Solar energy has an enormous potential for the heating and cooling of buildings, producing hot water for domestic and industrial purposes, cooking, warming greenhouses for agricultural crops, etc. However, solar energy is intermittent, unpredictable, and available only during the day. Hence, its application requires efficient thermal energy storage so that the surplus heat collected during sunshine hours may be stored for later use during the night. Similar problems arise in heat recovery

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systems, where the waste heat availability and utilization periods are different, requiring some thermal energy storage. In thermal energy storage, the useful energy from the collector is transferred to the storage medium where it is transformed into an internal energy. This may occur in the form of latent heat, sensible heat, or both. One major drawback of sensible heat storage is the large volume required, especially when the allowable temperature swing is small. Latent heat storage is more attractive than sensible heat storage because of its high storage density with smaller temperature swing (Lane, 1983; Abhat, 1983). However, many practical problems are encountered with latent heat storage due to low thermal conductivity, variation in thermo-physical properties under extended cycles, phase segression, subcooling, incongruent melting, volume change and high cost. These problems have to be technically resolved before latent heat storage can be widely used.

Latent heat storage is a relatively new area of research and pioneered by Dr. Telkes in the 1940s (Lane, 1983). It did not receive much attention, however, until the energy crisis of the late 1970s and early 1980s. PCM was first used in British trains against coolness. The first application of PCM described in the literature was their use for heating and cooling in buildings, by Telkes (1975), and Lane (1983). Telkes at al. (1978) published the idea of using PCMs in walls, better known as Trombe walls. Although research into latent heat storage for solar heating systems continues (Kaygusuz, 1999; Sari et al. 2000), it is increasingly being considered for waste heat recovery and load leveling for power generation (El- Dessouky et al. 1997).

The present paper is a compilation of much of practical information on various PCMs and latent heat storage systems. This review will help to find the suitable PCM for various purposes, suitable heat exchangers with ways to enhance the heat transfer, and it will also help to provide a variety of designs to store heat using PCMs for different applications, i.e. space heating & cooling, solar cooking, greenhouses, solar water heating and waste heat recovery systems. Thermo-physical property measurement techniques, thermal cycles testing for stability and enhancement of heat transfer in PCMs are discussed in this paper.

ENERGY STORAGE METHODS

The different forms of energy that can be stored include mechanical, electrical, and thermal energy. Mechanical energy storage systems include gravitational energy storage or Pumped Hydro Power Storage (PHPS), Compressed Air Energy Storage (CASE) and Flywheels. The PHPS and CAES technologies can be used for large-scale utility energy storage while flywheels are more suitable for intermediate storage. Energy storage through batteries is an option for storing the electrical energy. A battery is 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. Potential applications of batteries are utility peak shaving, load leveling, and storage of electrical energy generated by wind turbine or photovoltaic plants. The most common type of storage battery is the lead acid and Ni - Cd batteries.

Thermal energy can be stored as a change in internal energy of a material as sensible heat, latent heat, and thermo-chemical heat, or combination of these. In Sensible Heat Storage (SHS), thermal energy is stored by raising the temperature of a solid or liquid. SHS systems utilize the heat capacity and the change in temperature of the material during the process of charging and discharging. The amount of stored heat depends on the specific heat of the medium, the temperature change, and the amount of storage material.

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

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. The storage capacity of the LHS system with a PCM medium is given by

$$\begin{aligned} Q &= m a_m \Delta h_m + \int_i^m m C_p dT + \int_m^f m C_p dT \\ &= m\left[a_m \Delta h_m + C_{sp}(T_m - T_i) + C_{lp}(T_f - T_m)\right] \end{aligned} \tag{2}$$

LHS systems have certain benefits in comparison with SHS systems. The most important is the higher energy density per unit mass and per unit volume.

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

$$Q = a_r m \Delta h_r \tag{3}$$

Amongst thermal heat storage techniques, latent heat thermal energy storage is particularly attractive due to its ability to provide high energy storage density and its characteristics to store heat at constant temperature corresponding to the phase transition temperature of the PCM.

Latent heat storage can be accomplished through solid-liquid, liquid-gas, solid-gas and solid-solid phase transformations, but the only two of practical interest are the solid-liquid and solid-solid (Wang et al., 2000). Solid-gas and liquid-gas transition have a higher latent heat of fusion but their large volume changes on phase transition are associated with containment problems and rule out their potential utility in thermal storage systems. Large changes in volume make the system complex and impractical.

In solid–solid transitions, heat is stored when the material is transformed from one crystalline to another. This transition generally has smaller latent heat and volume changes than solid–liquid transition. Solid–solid PCMs offer the advantages of less rigorous container requirements and better design flexibility (Wang et al., 2000; Pillai et al., 1976). Most promising materials are organic solid solutions of pentaerythritol (melting point 188 °C, latent heat of fusion 323 kJ/kg), pentaglycerine (melting point 81°C, latent heat of fusion 216 kJ/kg), Li_2SO_4 (melting point 578 °C, latent heat of fusion 214 kJ/kg) and KHF_2 (melting point 196 °C, latent heat of fusion 135kJ/kg) (Garg et al. 1985). Trombe Walls with these materials could provide better performance than a plain concrete Trombe Wall.

Solid–liquid transformations have comparatively smaller latent heat than liquid-gas. However, these transformations involve only a small change in volume (< 10 %). Solid-liquid transition has proved to be economically attractive for use in thermal energy storage systems. PCMs themselves cannot serve as a heat transfer medium. Heat transfer mediums with a heat exchanger are required to transfer energy from the source to the PCM and from PCM to the load. Therefore, Designing of the heat exchanger is an important part for improving heat transfer in latent heat storage systems. PCMs also have positive volumetric expansion on melting, so, volume design of the containers is also necessary, which should be compatible with the PCM used. Any latent heat storage system must posses at least the following three properties: a suitable PCM with its melting point in the desired temperature range, a suitable heat exchange surface and a suitable container compatible with the PCM.

LATENT HEAT STORAGE MATERIALS

Phase Change Materials (PCM) are latent heat storage materials. As the source temperature rises, the chemical bonds within the PCM break up as the material changes phase from solid to liquid (as is the case for solid-liquid PCMs, which are of particular interest here). The phase change is a heat-seeking (endothermic) process and therefore, the PCM absorbs heat. Upon storing heat in the storage material, the material begins to melt when the phase change temperature is reached. The temperature then stays constant until the melting process is finished. The heat stored during the phase change process (melting process) of the material is called latent heat. Latent heat storage has two main advantages: (i) it is possible to store large amounts of heat with only small temperature changes and therefore to have a high storage density; (ii) because the change of phase at a constant temperature takes some time to complete, it becomes possible to smooth temperature variations. The comparison between latent and sensible heat storage shows that using latent heat storage, storage densities typically 5 to 10 times higher can be reached. PCM storage volume is two times smaller than that of water (Garg et al., 1985; Hasnain, 1998). Latent heat storage can be used in a wide temperature range. A large number of PCMs are known to melt with a heat of fusion in any required range. The PCM to be used in the design of thermal storage systems should accomplish desirable thermophysical, kinetics and chemical properties (Hale et al., 1971; Garg et al., 1985; Buddhi et al., 1994).

Thermo-physical Properties

(i) Melting temperature in the desired operating temperature range.
(ii) High latent heat of fusion per unit volume so that the required volume of the container to store a given amount of energy is less.
(iii) High specific heat to provide for additional significant sensible heat storage.
(iv) High thermal conductivity of both solid and liquid phases to assist the charging and discharging of energy of the storage systems.
(v) Small volume changes on phase transformation and small vapor pressure at operating temperatures to reduce the containment problem.
(vi) Congruent melting of the PCM for a constant storage capacity of the material with each freezing/melting cycle.

Kinetic Properties

(i) High nucleation rate to avoid super cooling of the liquid phase.
(ii) High rate of crystal growth, so that the system can meet demands of heat recovery from the storage system.

Chemical Properties

(i) Chemical stability.
(ii) Complete reversible freeze / melt cycle.
(iii) No degradation after a large number of freeze / melt cycles.
(iv) Non-corrosiveness to the construction materials.

(v) Non-toxic, non-flammable, and non-explosive materials for safety.

Moreover, low cost and large-scale availability of the PCMs is also very important.

Classification of PCMs

A classification of PCMs is given in Fig. 1. There are a large number of PCMs (organic, inorganic and eutectic), which can be identified as PCMs from the point of view melting temperature and latent heat of fusion. However, except for the melting point in the operating range, a majority of PCMs do not satisfy the criteria required for an adequate storage media as discussed in section 3.1. Organic and inorganic types of PCMs are given in Table 1 and 2 respectively. As no single material can have all the required properties for an ideal thermal storage media, one has to use the available materials and try to make up for the poor physical properties by an adequate system design. For example, metallic fins can be used to increase the thermal conductivity of PCMs, super-cooling may be suppressed by introducing a nucleating agent in the storage material, and incongruent melting can be inhibited by the use of a PCM of suitable thickness. For their very different thermal and chemical behavior, the properties of each sub-group, which affect the design of latent heat storage systems using PCMs of that sub-group, are discussed in detail below.

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 (Lane, 1983; Hale et al. 1971). It consists of mainly straight chain hydrocarbons that have melting temperatures ranging from 23 to 67 °C (Abhat, 1983). Commercial-grade paraffin wax is obtained from petroleum distillation and is not a pure substance, but a combination of different hydrocarbons. In general, the longer the average length of the hydrocarbon chain, the higher the melting temperature and heat of fusion (Hiran et al., 1994). Properties of some paraffins are given in Table 3. Paraffins are easily available from many manufacturers and are usually more expensive than salt hydrates (Lane, 1983; Hale et al., 1971).

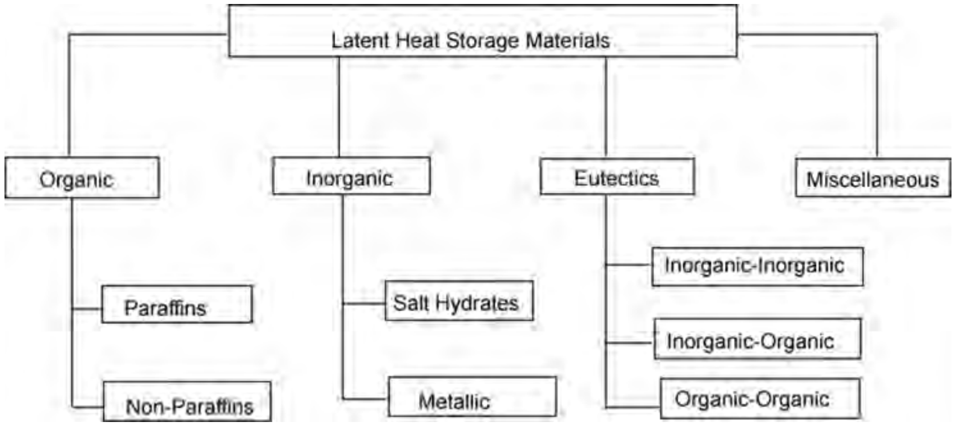

Figure 1 Classification of latent heat storage materials.

Table 1 List of Organic PCMs.

Material	Melting Point (°C)	Latent Heat (kJ/ kg)	Material	Melting Point (°C)	Latent Heat (kJ/ kg)
N-Tetradecane	5.5	226	N-Pentacosane	53.7	164
Formic acid	7.8	247	Myristic acid	54.0	199
N-Pentadecane	10.0	205	Oxolate	54.3	178
Acetic acid	16.7	273	Tristearin	54.5	191
N-Hexadecane	16.7	237	O-Xylene dichloride	55.0	121
Caprilone	40.0	260	β Chloroacetic acid	56.0	147
Docasyle bromide	40.0	201	N-Hexacosane	56.3	255
N-Henicosane	40.5	161	Nitro naphthalene	56.7	103
Phenol	41.0	120	α Chloroacetic acid	61.2	130
N-Lauric acid	43.0	183	N-Octacosane	61.4	134
P-Joluidine	43.3	167	Palmitic acid	61.8	164
Cynamide	44.0	209	Bees wax	61.8	177
N-Docosane	44.5	157	Glyolic acid	63.0	109
N-Tricosane	47.6	130	P-Bromophenol	63.5	86
Hydrocinnamic acid	48.0	118	Azobenzene	67.1	121
Cetyl alcohol	49.3	141	Acrylic Acid	68.0	115
O-Nitroaniline	50.0	93	Dintro toluene (2,4)	70.0	111
Camphene	50.0	239	Phenylacetic acid	76.7	102
Diphenyl amine	52.9	107	Thiosinamine	77.0	140
P-Dichlorobenzene	53.1	121	Benzylamine	78.0	174

Hale et al., 1971; Lane, 1983; Garg et al., 1985; Buddhi, 1994; Sharma, 1999; Gustafsson et al., 1998; Zalba et al., 2003; Farid et al., 2004.

Table 2 List of Inorganic PCMs.

Name	Melting Point (°C)	Latent Heat (kJ/kg)	Name	Melting Point (°C)	Latent Heat (kJ/kg)
H_2O	0.0	333	BI_3	31.8	10
$POCl_3$	1.0	85	$SO_3(\beta)$	32.3	151
D_2O	3.7	318	$TiBr_4$	38.2	23
$SbCl_5$	4.0	33	$H_4P_2O_6$	55.0	213
H_2SO_4	10.4	100	$SO_3\ (\gamma)$	62.1	331
IC l (β)	13.9	56	$SbCl_3$	73.4	25
MOF_6	17.0	50	$NaNO_3$	307	199
SO3(α)	17.0	108	KNO_3	380	266
IC l (α)	17.2	69	KOH	380	149
P_4O_6	23.7	64	$MgCl_2$	800	492
H_3PO_4	26.0	147	NaCl	802	492
Cs	28.3	15	Na_2CO_3	854	275
Ga	30.0	80	KF	857	452
$AsBr_3$	30.0	38	K_2CO_3	897	235
$SnBr_4$	30.0	28			

Lane, 1983; Abhat, 1983; Garg et al., 1985; Buddhi, 1994; Hale et al., 1971; Sharma, 1999.

Advantages. Paraffin waxes show no tendency to segregate. They are chemically stable, although Lane (1983) reports slow oxidation when exposed to oxygen, therefore, they required closed containers. Sharma et al. (1999; 1998; 2002) report stable properties after 1500 cycles in commercial-grade paraffin wax. Paraffin wax did not show regular degradation in thermal properties after repeated melting / freezing cycles. Paraffin waxes show high heats of fusion, as shown in Table 3. They also have no tendencies to super

Table 3 Melting Point and Latent Heat of Fusion of Paraffins.

Name	No. of "C" Atoms	Melting Point (°C)	Density (kg/m^3)	Thermal Conductivity (W/mK)	Latent Heat (kJ/kg)
n - Dodecane	12	–12	750	0.21^S	n.a.
n - Tridecane	13	–6	756		n.a.
n - Tetradecane	14	4.5–5.6	771		231
n - Pentadecane	15	10	768	0.17	207
n - Hexadecane	16	18.2	774	0.21^S	238
n - Heptadecane	17	22	778		215
n - Octadecane	18	28.2	814^S[14], 775^L [14]	0.35^S [14], 0.149^L[14]	245
n - Nonadecane	19	31.9	912^S, 769^L	0.21^S	222
n - Eicosane	20	37			247
n - Heneicosane	21	41			215
n - Docosane	22	44			249
n - Tricosane	23	47			234
n - Tetracosane	24	51			255
n - Pentacosane	25	54			238
Paraffin wax	n.a.	32	785^S[15], 749^L[15]	0.514^S[15], 0.224^L[15]	251[15]
n - Hexacosane	26	56	770	0.21^S	257
n - Heptacosane	27	59	773		236
n - Octacosane	28	61	910^S, 765^L		255
n - Nonacosane	29	64			240
n - Triacontane	30	65			252
n - Hentriacontane	31	n.a.	930^S, 830^L		n.a.
n - Dotricontane	32	70			n.a.
n - Tritricontane	33	71			189

S: solid; L: liquid; n.a.: not available.

Lane, 1983; Abhat, 1983; Garg et al., 1985; Buddhi, 1994; Hale et al., 1971; Sharma, 1999.

cool, so nucleating agents are not necessary (Lane, 1983; Buddhi et al., 1994). Paraffin waxes are safe and non-reactive (Hale et al., 1971; Hasnain, 1998). They are compatible with all metal containers and easily incorporated into heat storage systems (Lane, 1983). Care should be taken when using plastic containers as paraffins have a tendency to infiltrate and soften some plastics (Lane, 1983).

Disadvantages. Paraffins have low thermal conductivity in their solid state, as can be seen from Table 4. This presents a problem when high heat transfer rates are required during the freezing cycle. Velraj et al. (1998) reports that this problem can be decreased using finned containers and metallic fillers, or through a combination of latent/sensible storage systems. Aluminum honeycombs have been found to improve system performance (Hale et al., 1971). Paraffins have a high volume change between the solid and liquid stages. This causes many problems in container design (Hasnain, 1998). Lane (1983) also reports that paraffins greatly decrease heat storage capacity. Unlike Salt Hydrates, commercial paraffins generally do not have sharp, well-defined melting points. Paraffins are flammable, but this can be easily alleviated by a proper container (Hiran et al., 1994; Hale et al., 1971; Hasnain, 1998).

Non-paraffins

This is the largest category of candidate materials for latent heat storage. Lane (1983; 1989), Abhat (1983) and Buddhi et al. (1994) have conducted an extensive survey

Table 4 Melting Point and Latent Heat of Fusion of Non - paraffins.

Name	Melting Point (°C)	Density (kg/m^3)	Latent Heat (kJ/ kg)
Formic acid	7.8	1226.7^{15C}	247
Acetic acid	16.7	1050^{20C}	187
Glycerin	17.9	1260^{20C}	198.7
Lithium chloride ethanolate	21	n.a.	188
Polyethylene glycol 600	20–25	1100^{20C}	146
D – Lattic acid	26	1249^{15C}	184
1-3 Methyl pentacosane	29	n.a.	197
Camphenilone	39	n.a.	205
Docasyl bromide	40	n.a.	201
Caprylone	40	n.a.	259
Heptadecanone	41	n.a.	201
1-Cyclohexylooctadecane	41	n.a.	218
4-Heptadacanone	41	n.a.	197
Cyanamide	44	1080^{20C}	209
Methyl eicosanate	45	851^{79C}	230
3-Heptadecanone	48	n.a.	218
2-Heptadecanone	48	n.a.	218
Camphene	50	842^{54C}	238
9-Heptadecanone	51	n.a.	213
Methyl behenate	52	n.a.	234
Pentadecanoic acid	52.5	n.a.	178
Hypophosphoric acid	55	n.a.	213
Chloroacetic acid	56	1580^{20C}	130
Trimyristin	33–57	862^{20C}	201–213
Heptaudecanoic acid	60.6	n.a.	189
Bee wax	61.8	950	177
Glycolic acid	63	n.a.	109
Oxazoline wax-TS 970	74	n.a.	
Arachic acid	76.5	n.a.	227
Bromcamphor	77	1449^{81C}	174
Durene	79.3	838^{20C}	156
Acetamide	81	1159	241
Methyl brombrenzoate	81	n.a.	126
Alpha napthol	96	$1095^{98.7C}$	163
Glautaric acid	97.5	1429	156
p-Xylene dichloride	100	n.a.	138.7
Methyl Fumarate	102	1045	242
Catechol	104.3	1370^{15C}	207
Quinone	115	1318^{20C}	171
Acetanilide	115	1210^{4C}	142
Succinic anhydride	119	1104	204
Benzoic acid	121.7	1266^{15C}	142.8
Stibene	124	1164^{15C}	167
Benzamide	127.2	1341	169.4
Phenacetin	137	n.a.	136.7
Alpha glucose	141	1544	174
Acetyl – p- toluidene	146	n.a.	180
Phenylhdrazone benzaldehyide	155	n.a.	134.8
Salicylic acid	159	1443^{20C}	199
Benzanilide	161	n.a.	162
O-Mannitol	166	1489^{20C}	294
Hydroquinone	172.4	1358^{20C}	258
p-Aminobenzoic acid	187	n.a.	153

Lane, 1983; Abhat, 1983; Garg et al., 1985; Buddhi, 1994; Hale et al., 1971; Sharma, 1999.

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. Each of these materials will have its own 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. Non-paraffins are tabulated in Table 4.

Fatty Acids

Fatty acids, characterized by the chemical formula $CH_3(CH_2)_{2n}COOH$, have much the same characteristics as paraffins. Their advantage of sharper phase transformations is offset by the disadvantage of being about two or three times the cost of paraffins (Hasnain, 1998). They are mildly corrosive. Some fatty acids for low temperature latent heat storage applications are tabulated in Table 5. One promising use, given by Kauranen et al. (1991), is a system to combine fatty acids to obtain melting temperatures ranging from 20–30 °C with an accuracy of ± 0.5 °C. This would allow a designer to select the optimum operating temperature to obtain the maximum performance of a heat storage system. Sharma et al. (1999; 1998; 2002) have noticed that stearic acids melt over a wide range of temperature, have shown two melting points and have large variations in latent heat of fusion. But, they have thermally stable behavior after 1500 repeated melting / freezing cycles. The quality of stearic acid varies a lot in the commercial market due to their wide use in different products.

Table 5 Melting Point and Latent Heat of Fusion of Fatty Acids.

Name	Melting Point (°C)	Density (kg/m^3)	Thermal Conductivity (W/mK)	Latent Heat (kJ/kg)
Propyl palmiate	10	n.a.	n.a.	186
Isopropyl palmiate	11	n.a.	n.a.	100
Oleic acid	13.5–16.3	863^{60C}	n.a.	n.a.
Isopropyl stearate	14–19	n.a.	n.a.	140–142
Caprylic acid	16	901^{30C}	0.149^{39C}	148
	16.3	862^{80C} 981^{13C} 1033^{10C}	$0.145^{67.7C}$, 0.148^{20C}	149
Butyl stearate	19	n.a.	n.a.	140
				123–200
Dimethyl sabacate	21	n.a.	n.a.	120–135
Vinyl stearate	27–29	n.a.	n.a.	122
Methyl palmitate	29	n.a.	n.a.	205
Capric acid	32	878^{45C}	$0.153^{38.5C}$	152.7
	31.5	886^{40C}, 1004^{24C}	$0.152^{55.5C}$, 0.149^{40C}	153
Erucic acid	33	853^{70C}	n.a.	n.a.
Methyl-12-hydroxy-stearate	42–43	n.a.	n.a.	120–126
Lauric acid	42–44	862^{60C}, 1007^{24C}	n.a.	178
Elaidic acid	47	851^{79C}	n.a.	218
Pelargoinc acid	48	n.a.	n.a.	n.a.
Myristic acid	49–51	861^{55C}	n.a.	205
	54	844^{80C}		187
Palmitic acid	64	850^{65C}	$0.162^{68.4C}$	185.4
	61	847^{80C}	$0.159^{80.1C}$	203.4
Stearic acid	69	848^{70C}	0.172^{70C}	202.5
	60–61	965^{24C}		186.5
Valporic acid	120	n.a.	n.a.	n.a.

Lane, 1983; Abhat, 1983; Garg et al., 1985; Buddhi, 1994; Hale et al., 1971; Sharma, 1999.

Therefore, no guarantee can be provided for their purity. This may be the reason that the latent heats of fusion of stearic acid generally decrease with the number of thermal cycles.

Salt Hydrates

Salt hydrates are the oldest and most studied heat storage PCMs (Lane, 1983). They consist of a salt and water, which combine in a crystalline matrix when the material solidifies. They can be used alone or in eutectic mixtures (Abhat, 1983). Properties of some salt hydrates are given in Table 6. There are many different materials that have melting ranges of 15 to 117 °C (Lane, 1983). Salt hydrates are the most important group of PCMs, and have been extensively studied for their use in latent heat thermal energy storage systems. Three types of behavior of the melted salts can be identified: congruent, incongruent and semi-congruent melting. Congruent melting occurs when the anhydrous salt is completely soluble in its water of hydration at the melting temperature. Incongruent melting occurs when the salt is not entirely soluble in its water of hydration at the melting point. Semi-congruent melting occurs when the liquid and solid phases are in equilibrium during a phase transition.

Advantages. Low cost and easy availability of salt hydrates makes them attractive for heat storage applications (Lane, 1989). Two of the inexpensive and most available salt hydrates are $CaCl_2.6H_2O$ and $Na_2SO_4.10H_2O$ (Lane, 1983). Salt hydrates have a sharp melting point and high thermal conductivity when compared with other heat storage PCMs. This can increase heat transfer in and out of the storage unit. They have a high heat of fusion, which decreases the needed size of the storage system. Salt hydrates also show a lower volume change than other PCMs. This makes it easy to design a container to accommodate volume change.

Disadvantages. Segregation is a formation of other hydrates or dehydrated salts that tend to settle out and reduce the active volume available for heat storage. Abhat (1983) reports a decrease in heat of fusion of over 73% in $Na_2SO_4.10H_2O$ after 1000 melt/freeze cycles. This problem can be eliminated to a certain extent by using gelled or thickened mixtures (Lane, 1983), though this process negatively influences the heat storage characteristics of the mixture and the mixture still degrades with time (Abhat, 1983). Salt hydrates show super-cooling because they do not start to crystallize at the freezing point of other PCMs. This can be avoided using suitable nucleating materials to start crystal growth in the storage media. Lane (1983) offers a comprehensive listing of nucleating materials for most common salt hydrates. Abhat (1983) reports material degradation in $CaCl_2.6H_2O$ after only two cycles when the test sample was not hermetically sealed. Therefore, it is necessary to design containers to contain the material without letting water out. Another problem of salt hydrates is their tendency to cause corrosion in metal containers, which are commonly used in thermal storage systems (Abhat, 1983). Compatibility of a PCM and its container should always be checked before use.

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 (Lane, 1989). 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. A list of developed eutectics is given in Table 7.

Table 6 Melting point and latent heat of fusion of salt hydrates.

Name	Melting Point (°C)	Density (kg/m^3)	Thermal Conductivity (W/m K)	Latent Heat (kJ/kg)	Melting Behavior[a] [13]
$LiClO_3.3H_2O$	8	n.a.	n.a.	253	c
$NH_4Cl.Na_2SO_4.10H_2O$	11	n.a.	n.a.	163	n.a.
$K_2HO_4.6H_2O$	14	n.a.	n.a.	108	c
$NaCl.Na_2SO_4.10H_2O$	18	n.a.	n.a.	286	n.a.
$KF.4H_2O$	18	n.a.	n.a.	330	c
$K_2HO_4.4H_2O$	18.5	1447^{20C}, 1455^{18C}, 1480^{6C}	n.a.	231	n.a.
$Mn(NO_3)_2.6H_2O$	25 25.8	1738^{20C}[12], 1728^{40C}[12], 1795^{5C}[12]	n.a.	148 125.9[12]	n.a.
$LiBO_2.8H_2O$	25.7	n.a.	n.a.	289	n.a.
$FeBr_3.6H_2O$	27	n.a.	n.a.	105	n.a.
$CaCl_2.6H_2O$	29–30	1562^{32C}, 1802^{24C}	$0.561^{61.2C}$, 1.008^{23C}	170–192	ic
$LiNO_3.3H_2O$	30	n.a.	n.a.	189–296	c
$Na_2SO_4.10H_2O$	32	1485^{24C}	0.544	251–254	ic
$Na_2CO_3.10H_2O$	33–36	1442	n.a.	247	ic
$KFe(SO_4)_2.12H_2O$	33	n.a.	n.a.	173	ic
$CaBr_2.6H_2O$	34	1956^{35C}, 2194^{24C}	n.a.	115–138	n.a.
$LiBr.2H_2O$	34	n.a.	n.a.	124	ic
$Na_2HPO_4.12H_2O$	35	1522	n.a.	256–281	ic
$Zn(NO_3)_2.6H_2O$	36	1828^{36C}, 1937^{24C}, 2065^{14C}	$0.464^{39.9C}$, $0.469^{61.2C}$	134–147	c
$Mn(NO_3)_2.4H_2O$	37	n.a.	n.a.	115	n.a.
$FeCl_3.6H_2O$	37	n.a.	n.a.	223	c
$CaCl_2.4H_2O$	39	n.a.	n.a.	158	ic
$CoSO_4.7H_2O$	40.7	n.a.	n.a.	170	n.a.
$CuSO_4.7H_2O$	40.7	n.a.	n.a.	171	n.a.
$KF.2H_2O$	42	n.a.	n.a.	162–266	c
$MgI_2.8H_2O$	42	n.a.	n.a.	133	n.a.
$CaI_2.6H_2O$	42	n.a.	n.a.	162	n.a.
$Ca(NO_3)_2.4H_2O$	43–47	n.a.	n.a.	106–140	c
$Zn(NO_3)_2.4H_2O$	45	n.a.	n.a.	110	n.a.
$K_3PO_4.7H_2O$	45	n.a.	n.a.	145	n.a.
$Fe(NO_3)_3.9H_2O$	47	n.a.	n.a.	155–190	ic
$Mg(NO_3)_3.4H_2O$	47	n.a.	n.a.	142	n.a.
$Na_2SiO_3.5H_2O$	48	n.a.	n.a.	168	n.a.
$Na_2HPO_4.7H_2O$	48	n.a.	n.a.	135–170	ic
$Na_2S_2O_3.5H_2O$	48	1600	n.a.	209	n.a.
$K_2HPO_4.3H_2O$	48	n.a.	n.a.	99	n.a.
$MgSO_4.7H_2O$	48.4	n.a.	n.a.	202	n.a.
$Ca(NO_3)_2.3H_2O$	51	n.a.	n.a.	104	n.a.
$Na(NO_3)_2.6H_2O$	53	n.a.	n.a.	158	n.a.
$Zn(NO_3)_2.2H_2O$	55	n.a.	n.a.	68	c
$FeCl_3.2H_2O$	56	n.a.	n.a.	90	n.a.
$CO(NO_3)_2.6H_2O$	57	n.a.	n.a.	115	n.a.
$Ni(NO_3)_2.6H_2O$	57	n.a.	n.a.	168	n.a.
$MnCl_2.4H_2O$	58	n.a.	n.a.	151	n.a.

Table 6 Continued

Name	Melting Point (°C)	Density (kg/m^3)	Thermal Conductivity (W/m K)	Latent Heat (kJ/kg)	Melting Behavior^a [13]
$CH_3COONa.3H_2O$	58	n.a.	n.a.	270–290	ic
$LiC_2H_3O_2.2H_2O$	58	n.a.	n.a.	251–377	n.a.
$MgCl_2.4H_2O$	58.0	n.a.	n.a.	178	n.a.
$NaOH.H_2O$	58	n.a.	n.a.	272	n.a.
$Na(CH_3COO).3H_2O$	58	n.a.	n.a.	n.a.	n.a.
$Cd(NO_3)_2.4H_2O$	59	n.a.	n.a.	98	n.a.
$Cd(NO_3)_2.1H_2O$	59.5	n.a.	n.a.	107	n.a.
$Fe(NO_3)_2.6H_2O$	60	n.a.	n.a.	125	n.a.
$NaAl(SO_4)_2.12H_2O$	61	n.a.	n.a.	181	ic
$FeSO_4.7H_2O$	64	n.a.	n.a.	200	n.a.
$Na_3PO_4.12H_2O$	65	n.a.	n.a.	168	n.a.
$Na_2B_4O_7.10H_2O$	68	n.a.	n.a.	n.a.	n.a.
$Na_3PO_4.12H_20$	69	n.a.	n.a.	n.a.	n.a.
$LiCH_3COO.2H_2O$	70	n.a.	n.a.	150–251	c
$Na_2P_2O_7.10H_2O$	70	n.a.	n.a.	186–230	ic
$Al(NO_3)_2.9H_2O$	72	n.a.	n.a.	155–176	ic
$Ba(OH)_2.8H_2O$	78	1937^{84C}, 2070^{24C}, 2180	$0.653^{85.7C}$, $0.678^{98.2C}$, 1.255^{23C}	265–280	c
$Al_2(SO_4)_3.18H_2O$	88	n.a.	n.a.	218	ic
$Sr(OH)_2.8H_2O$	89	n.a.	n.a.	370	ic
$Mg(NO_3)_2.6H_2O$	89–90	1550^{94C}, 1636^{25C}	0.490^{95C}, 0.502^{110C}, 0.611^{37C}, $0.669^{55.6C}$	162–167	c
$KAl\ (SO_4)_2.12H_2O$	91	n.a.	n.a.	184	n.a.
$(NH_4)Al(SO_4).6H_2O$	95	n.a.	n.a.	269	n.a.
$Na_2S.51/2H_2O$	97.5	n.a.	n.a.	n.a.	n.a.
$LiCl.H_2O$	99	n.a.	n.a.	212	ic
$CaBr_2.4H_20$	110	n.a.	n.a.	n.a.	n.a.
$Al_2(SO_4)_2.16H_2O$	112	n.a.	n.a.	n.a.	n.a.
$MgCl_2.\ 6H_2O$	115–117	1450^{120C}, 1442^{78C}, 1569^{20C}, 1570^{20C}	0.570^{120C}, 0.598^{140C}, 0.694^{90C}, 0.704^{110C}	165–169	n.a.
$NaC_2H_3O_2.3H_2O$	137	1450	n.a.	172	n.a.

n.a.: not available; c: congruent melting; ic: incongruent melting.

Lane, 1983; Abhat, 1983; Garg et al., 1985; Buddhi, 1994; Hale et al., 1971; Sharma, 1999.

Cross-linked Polyethylene

Cross-linked polyethylene is much like the polyethylene used in plastic bottles, except for the fact that it is lightly cross-linked to prevent it from turning into a liquid when it melts. Like a liquid-solid PCM, it stores energy in the forming and breaking of its crystalline structure. Properties of two cross-linked polyethylenes are shown in Table 8. Cross-linked polyethylene is more stable than a liquid-solid PCM and can be used without encapsulation in another material.

Advantages. Although higher in cost than other PCMs, they do not need encapsulation. Therefore, low cost is attained for the entire heat storage system, and there are more

Table 7 List of Organic and Inorganic Eutectics.

Name	Composition (wt %)	Melting Point (°C)	Latent Heat (kJ/ kg)
Na_2SO_4+NaCl+KCl+H_2O	31+13+16+40	4	234
Na_2SO_4+NaCl+NH_4Cl+H_2O	32+14+12+42	11	n.a.
$C_5H_5C_6H_5$+ $(C_6H_5)_2O$	26.5+73.5	12	97.9
Na_2SO_4+NaCl+H_2O	37+17+46	18	n.a.
Na_2S_4+$MgSO_4$+H_2O	25+21+54	24	n.a.
$C_{14}H_{28}O_2$+$C_{10}H_{20}O_2$	34+66	24	147.7
$Ca(NO)_3.4H_2O$+$Mg(NO)_3.6H_2O$	47+53	30	136
NH_2CONH_2+NH_4 NO_3	–	46	95
$Mg(NO_3)_2.6H_2O$+NH_4 NO_3	61.5+38.4	52	125.5
$Mg(NO_3)_2.6H_2O$+$MgCl_2.6H_2O$	58.7+41.3	59	132.2
$Mg(NO_3)_2.6H_2O$+$Al(NO_3)_2.9H_2O$	53+47	61	148
$Mg(NO_3)_2.6H_2O$+$MgBr_2.6H_2O$	59+41	66	168
Napthalene + Benzoic Acid	67.1+32.9	67	123.4
$AlCl_3$+NaCl+$ZrCl_2$	79+17+4	68	234
$AlCl_3$+NaCl+KCl	66+20+14	70	209
NH_2CONH_2+NH_4Br	66.6+33.4	76	151
$LiNO_3$ + NH_4 NO_3+$NaNO_3$	25+65+10	80.5	113
$AlCl_3$+NaCl+KCl	60+26+14	93	213
$AlCl_3$+NaCl	66+34	93	201
$NaNO_2$+$NaNO_3$+KNO_3	40+7+53	142	n.a.

n.a.: not available.

Lane, 1983; Abhat, 1983; Garg et al., 1985; Buddhi, 1994; Hale et al., 1971; Sharma, 1999.

Table 8 Melting Point and Latent Heat of Fusion of Some Selected Solid - Solid PCMs.

Name	Melting Point (°C)	Latent Heat (kJ/kg)
38.2%NPG/61.8%PE	26–32	18–75
38.2%NPG/61.8%TAM	22–35	27–33
76.4%NPG/33.6%TAM	28–38	75–80
76.4%NPG/33.6%PE	31–37	35–46
91%NPG/9%PE	31–36	68
91%NPG/9%TAM	30–39	143–150
Neopentyl glycol (NPG)	43	130
Diamnopentacrythritol	68	184
2-Amino - 2 - methyl - 1, 3 - propanediol	78	264
2 - Methyl - 2 - mtro - 1, 3 - propanediol	79	201
Trumethylolethane	81	192
Pentaglycerin	81	192
2-Hydroxymethyl-2-methyl-1, 3 - propanediol	81	192
Monoaminopentaerythritol	86	192
Cross-linked polyethylene	110–115	125–146
Tris(Hydroxymethyl)acetic acid	124	205
2-Amino-2-hydroxymethyl-1, 3 - propanediol	131	285
Cross-linked HDPE	125–146	167–201
2,2-Bis(Hydroxymethyl) Propionic acid	152	289
38.2%NPG/61.8%PE	170	147
Penterythritol (PE)	185	303

Lane, 1983; Abhat, 1983; Garg et al., 1985; Buddhi, 1994; Hale et al., 1971; Sharma, 1999.

feasibilities than with other PCMs. Cross-linked polyethylene is non-toxic and mostly chemically inert.

Disadvantages. The operating temperatures of 110 to 140 °C are too high for some applications such as space heating and water heating. To the author's knowledge, no company has commercially developed cross-linked polyethylene for heat storage applications at present.

Polyalcohols

Polyalcohols store energy in a structure change from a heterogeneous state at lower temperatures to a face-centered cubic form at higher temperatures (Wang et al, 2000). Polyalcahols have many advantages over solid-liquid PCMs, such as small volume change, no leaking, and no degradation of the material (Wang et al, 2000). These advantages come with the disadvantages of low latent heat, high phase-change temperatures, and higher cost. Wang et al. (2000) reports a system of combining polyalcohols to adjust working temperatures. Some of his results are shown in Table 8 for Neopentyl Glycol (NPG)/ Penaerythritol (PE) and Neopentyl Glycol (NPG)/Trihydroxy Mthyl-Aminomethane (TAM) systems.

Commercial PCMs

Many companies (Climator, Cristopia, EPS Ltd., Mitsubishi Chemical Corporation, Rubitherm GmbH TEAP and Witco) are engaged in the development of PCMs for several applications. We tried to compile the commercially available PCMs for the temperature range 0 °C - 118 °C, and these are tabulated in Table 9.

LATENT HEAT STORAGE SYSTEMS

The intermittent and dynamic nature of solar irradiance and the need to utilize solar energy systems in a continuous and static load make the use of storage systems essential in most of the potential uses of solar energy. The use of PCMs can be found in solar energy storage systems for water heating, green houses, space heating and cooling, cooking and waste heat recovery systems.

Solar Water Heater

Solar water heaters are getting popular (Buddhi et al., 1987; Tanishita, 1970) because they are relatively inexpensive and simple to fabricate and maintain. Prakesh et al. (1985) analyzed a built-in-storage type water heater containing a layer of PCM at the bottom (Fig. 2). During sunshine hours, the water gets heated, which in turn transfers heat to the PCM below it. The PCM melts and collects energy in the form of latent heat. During non-sunshine hours, the hot water is withdrawn and is substituted by cold water, which gains energy from the PCM. The energy is released by the PCM when changing its phase from liquid to solid. This type of system may not be effective due to the poor heat transfer between PCMs and water. Bansal and Buddhi (1992a) conducted an analytical study on cylindrical latent heat storage systems for domestic hot water (Fig. 3). During the charging mode of the PCM, the cylindrical capsule is in the closed loop with a solar water heater, and during the discharging mode, a liquid flowing through the storage unit extracts the energy. As a result, a theoretical model for a cylindrical latent heat storage system was

Table 9 List of Commercially Available PCMs (0 °C–118 °C).

Name	Melting Point (°C)	Latent Heat (kJ/kg)	Density (kg/m^3)	Manufacturer
TH 0	0	334	n.a.	TEAP (www.teappcm.com)
A 4	4	227	766	EPS Ltd. (www.epsltd.co.uk)
Witco 85010-1	4	129.6	n.a.	Witco
RT 2	6	156	860	Rubitherm (www.rubitherm.com)
TH 7	7	189	n.a.	TEAP (www.teappcm.com)
RT 5	7	156	860	Rubitherm (www.rubitherm.com)
E 7	7	120	1540	EPS Ltd. (www.epsltd.co.uk)
C 7	7	162	1420	Climator (www.climator.com)
RT 6	8	174	860	Rubitherm (www.rubitherm.com)
E 8	8	140	1470	EPS Ltd. (www.epsltd.co.uk)
A 8	8	220	770	EPS Ltd. (www.epsltd.co.uk)
E 10	10	140	1520	EPS Ltd. (www.epsltd.co.uk)
E 13	13	140	1780	EPS Ltd. (www.epsltd.co.uk)
C 15	15	130	n.a.	Climator (www.climator.com)
E 21	21	150	1480	EPS Ltd. (www.epsltd.co.uk)
RT 20	22	172	870	Rubitherm (www.rubitherm.com)
A 22	22	220	770	EPS Ltd. (www.epsltd.co.uk)
C 24	24	216	1480	Climator (www.climator.com)
RT 26	25	131	880	Rubitherm (www.rubitherm.com)
TH 25	25	159	n.a.	TEAP (www.teappcm.com)
Witco 45 A	26.3	167.2	n.a.	Witco
S 27	27	207	1470	Cristopia (www.cristopia.com)
STL 27	27	213	1090	Mitsubishi Chemical
RT 27	28	179	870	Rubitherm (www.rubitherm.com)
GR 27	28	72	750	Rubitherm (www.rubitherm.com)
PX 27	28	112	640	Rubitherm (www.rubitherm.com)
A 28	28	245	790	EPS Ltd. (www.epsltd.co.uk)
TH 29	29	188	1540	TEAP (www.teappcm.com)
E 30	30	201	1300	EPS Ltd. (www.epsltd.co.uk)
C 32	32	302	1450	Climator (www.climator.com)
E 32	32	186	1460	EPS Ltd. (www.epsltd.co.uk)
RT 35	35	157	880	Rubitherm (www.rubitherm.com)
RT 42	43	174	880	Rubitherm (www.rubitherm.com)
GR 41	43	63	750	Rubitherm (www.rubitherm.com)
FB 41	43	117	750	Rubitherm (www.rubitherm.com)
RT 41	43	152	880	Rubitherm (www.rubitherm.com)
STL 47	47	221	1340	Mitsubishi Chemical
E 48	48	201	1670	EPS Ltd. (www.epsltd.co.uk)
C 48	48	324	1360	Climator (www.climator.com)
STL 52	52	201	1300	Mitsubishi Chemical
PX 52	53	103	640	Rubitherm (www.rubitherm.com)
STL 55	55	242	1290	Mitsubishi Chemical
FB 54	55	135	750	Rubitherm (www.rubitherm.com)
RT 54	55	179	900	Rubitherm (www.rubitherm.com)
E 58	58	226	1280	EPS Ltd. (www.epsltd.co.uk)
C 58	58	364	1460	Climator (www.climator.com)
TH 58	58	226	1290	TEAP (www.teappcm.com)
RT 65	64	173	910	Rubitherm (www.rubitherm.com)
C 70	70	194	1700	Climator (www.climator.com)
PX 80	77	91	640	Rubitherm (www.rubitherm.com)
GR 80	79	71	750	Rubitherm (www.rubitherm.com)
FB 80	79	132	750	Rubitherm (www.rubitherm.com)
RT 80	79	175	920	Rubitherm (www.rubitherm.com)

Table 9 Continued

Name	Melting Point (°C)	Latent Heat (kJ/kg)	Density (kg/m^3)	Manufacturer
PCM 80	80	231	n.a.	Mitsubishi Chemical
PCM 86	86	246	n.a.	Mitsubishi Chemical
E 89	89	163	n.a.	EPS Ltd. (www.epsltd.co.uk)
TH 89	89	149	n.a.	TEAP (www.teappcm.com)
RT 90	90	194	930	Rubitherm (www.rubitherm.com)
RT 100	99	168	940	Rubitherm (www.rubitherm.com)
RT 112	112	213	n.a.	Rubitherm (www.rubitherm.com)
E 117	117	169	1450	EPS Ltd. (www.epsltd.co.uk)
?	118	339.8	1480	Mitsubishi Chemical

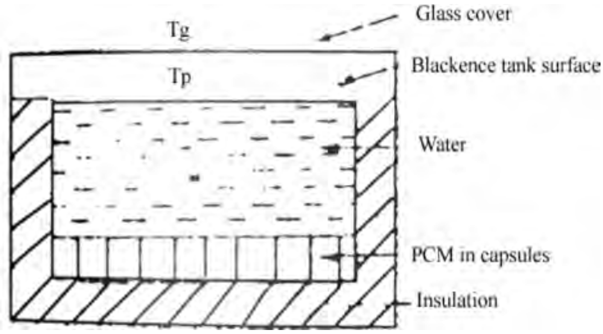

Figure 2 Built-in storage-type heater with PCM layer.

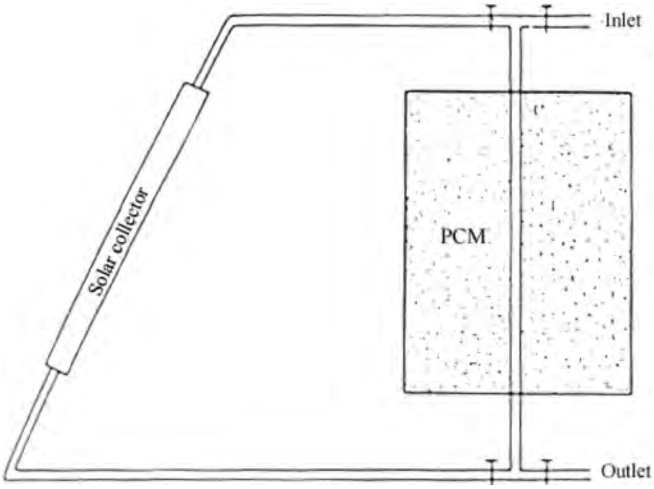

Figure 3 A domestic hot water system with separate latent heat storage unit.

developed. The calculations for the interface-moving boundary and fluid temperature were made by using paraffin wax (p-116) and stearic acid as PCMs.

Tiwari et al. (1998) presented an analysis of PCM storage for a water heater by incorporating the effect of water flow through a parallel plate placed at the solid-liquid interface. In order to reduce the night heat losses from the exposed surface, a provision of covering the system by movable insulation was made. They concluded that the hot water (temperature 15–20 °C > ambient air temperature) can remain throughout the day and night, and the fluctuations in water temperature decrease with an increase in the melted region of the PCM water heater. Tayeb et al. (1993) developed a system for domestic hot water using $Na_2SO_4.10H_20$ as a PCM and compared it with the simulation model that gives the optimum flow rate of the inlet water supply required to maintain the constant-temperature water at the outlet. Font et al. (1994) conducted a preliminary study for the design of a device for a domestic water heater using a solid-solid PCM. Numerical simulation has been made using a unidirectional model and verified with the experimental results. The concordance between both experimentally and simulation results shows that this model is available to study the heat transfer phenomenon in the PCM in order to optimize the design of the device.

Chauarsia (1986) and Gu et al. (2004) reported that paraffin wax could be used as a storage system for solar water heating. Baran and Sari (2003) reported the eutectic (melting point 52.3 °C, latent heat of fusion 182 kJ/kg) of palmitic acid (64.2 wt%) plus stearic acid (35.8 wt%) is suitable for domestic water heating applications. Bhargava (1983) utilized the PCM for a solar water heater and concluded that the efficiency of the system and the outlet water temperature during the evening hours increases with the increase in the thermal conductivity of the solid-liquid phases of the materials. Hasan et al. (1994) has investigated some fatty acids as PCMs for domestic water heating. They recommended that myristic acid, palmitic acid and stearic acid, with melting temperature between 50 °C - 70 °C are the most promising PCMs for water heating. They concluded that a little reduction of the latent heat was found after 450 heating cycles.

Kurklu et al. (2002) designed, developed and evaluated the thermal performance of a new type of water-PCM solar collector. The solar collector consisted of two adjoining sections, one filled with water and the other with a paraffin wax (50 °C) as a PCM (Fig. 4). The results of the study indicated that the water temperature exceeded 55 °C during a typical day of high solar irradiance and it was kept over 30 °C for the whole night. This water-PCM solar collector has many advantages over the traditional solar hot water collectors in Turkey in terms of total system weight, cost and energy storage applications.

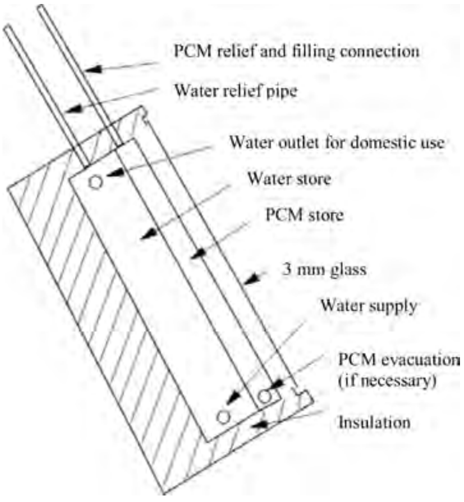

Figure 4 Water – PCM solar collector.

Recently, Canbazoglu et al. (2004) compared solar water heating systems with PCMs to conventional solar water heating systems. Fig. 5 shows a detailed cross-sectional view of a heat storage tank combined with a PCM. Polyethylene bottles were filled with a PCM and set into the tank as three rows. The total mass of PCM used in the heat storage tank was approximately 180 kg, using the density of the solid state of the PCM of 1666 kg/m^3. The bottles do not let the water flow in a horizontal direction due to their close location. Water flows through the vertical cavities between the bottles in the heat storage tank. The results indicate that the water temperature has a constant value of 46 °C during the night until sunrise, as the hot water was not consumed. The difference between the temperatures at the midpoint of the heat storage tank and at the outlet of the collector of the heat storage tank with the PCM is greater, by an average value of approximately 6 °C, than that of the system without a PCM. This temperature difference is considerable, exhibiting the high heat storage performance of the heat storage system with a PCM, during November. The storage time of hot water, the mass of hot water produced to use, and the total heat accumulated in the heat storage tank that contains some hydrated salts (used in the present study) are approximately 2.59–3.45 times greater than that of conventional solar energy systems with a heat storage tank that does not include a PCM. The thermal performances of hydrated salt-PCMs such as $Na_2S_2O_3.5H_2O$, $Zn(NO_3)_2.6H_2O$, $Na_2HPO_4.12H_2O$, $CaCl_2.6H_2O$ and $Na_2SO_4.10H_2O$ were examined theoretically. The hydrated salts with the highest solar thermal energy storage performance are $Na_2HPO_4.12H_2O$ and $Na_2SO_4.10H_2O$. The additional cost for a PCM comes to around $ 0.5 US per the unit volume of the heat storage tank in liters. However, the volume of a hot water tank required to store the same heat in energy storage systems including a PCM will be smaller than that of conventional solar energy storage systems. Therefore, it is obvious that the use of PCMs in the system may not cause an important increase in cost.

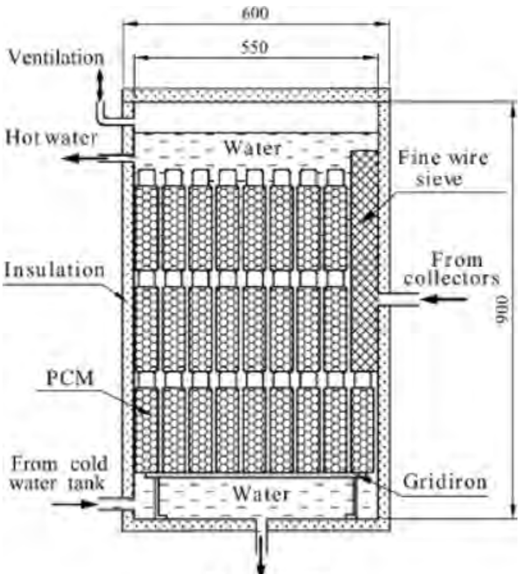

Figure 5 A cross-sectional view of the cylindrical heat storage tank combined with PCM.

Space Heating

Jurinak and Khalik (1978; 1979) have studied the effects of PCMs on the performance of an air-based solar heating system. Their main conclusion was that the PCM should be selected based on its melting temperature, rather than its latent heat, i.e., melting temperature has a significant effect on system performance. They also reported that systems utilizing $Na_2SO_4.10H_20$ require roughly one-half the storage volume of a conventional water tank system. An effective heat capacity for the latent heat storage unit was also obtained as a function of its mass, latent heat, specific heat, and melting temperature. Acquired effective heat capacity could be used to estimate the thermal performance of the system utilizing a PCM. Klein and Beckman (1979) presented a simulation study for a closed-loop solar thermal system, which could be used for a variety of applications including space heating, absorption air conditioning, and certain types of process heating. This design method can be used to estimate the long-term performance of such system type. Bulkin et al. (1988) suggested a mathematical model for designing a solar heating and hot water supply system on the basis of solar absorbers and a heat pump with two thermal-storage tanks, taking into account the system's interaction with the outside climate and with the room being served. Ghoneim (1989) has studied the effect of assumptions in the models of earlier studies on both the fraction of the load met by solar energy, and the required storage capacities.

Kaygusuz et al. (1991) set up an experimental model to determine the performance of solar-assisted heat pumps, collectors, dryers, and energy storage tanks used for drying grains. Kaygusuz (1995a) examined the performance of a dual-source heat pump system for residential heating (Fig.6). In the dual-source configuration, the evaporator is designed to receive energy from the atmosphere or from the solar energy store. He concluded that the dual source system could save more energy than the parallel and series system. Kaygusuz (1995b) also carried out an experimental and theoretical study to determine the performance of PCM storage, and the variation of the outlet fluid temperature with different values of NTU (the number of transfer units of the storage unit) for water-based solar heating systems. This system contained a solar collector, energy storage tank, water-to-air heat exchanger, auxiliary electrical heater, water circulating pump and other measuring

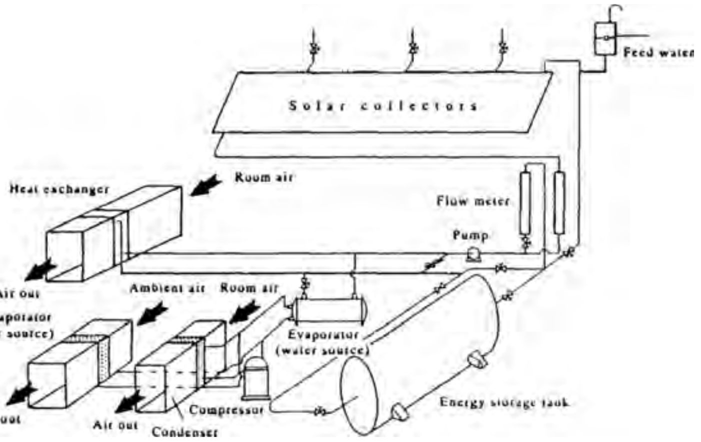

Figure 6 Solar-assisted heat pump system with energy storage tank.

and control equipment (Fig.7). Whenever solar energy is available, it is collected and transferred to the energy storage tank that is filled with 1500 kg encapsulated PCM, and heat transfer fluid (water) flows parallel to them (Fig.8). From the experimental and theoretical investigations, they concluded that heat storage is an important component in moderate climatic conditions (i.e., Trabzon, Turkey), and for this purpose, $CaCl_2.6H_20$ or $Na_2SO_4.10H_2O$ can be used as a PCM and would provide a desirable alternative to rock and water storage systems. PCM storage is preferable as a heat source than the water and rock storage for a heat pump because the energy storage temperature of the PCM is around 25–35°C for either $CaCl_2.6H_20$ or $Na_2SO_4.10H_2O$. This temperature range is suitable for solar-assisted heat pump applications in Turkey.

Mehmet (2000) also evaluated the thermal performance of a cylindrical storage tank linked to a solar powered heat pump used for space heating with a heat pump. This system was designed to heat the 75 m^2 floor area (Fig.9). A cylindrical latent heat storage tank was connected to a solar collector (30 m^2). The storage tank was filled with 1090 kg encapsulated PCM ($CaCl_2.6H_20$). The storage tank was packed vertically with cylindrical tubes containing PCM, as shown in Fig. 9. During the charging mode, water receives solar energy from the collector and heats up, then goes to the storage tank. It then transfers some energy to the PCM in the storage tank. After this procedure, it is used as a heat source by the water-sourced evaporator of the heat pump. Finally, it is sent to the solar

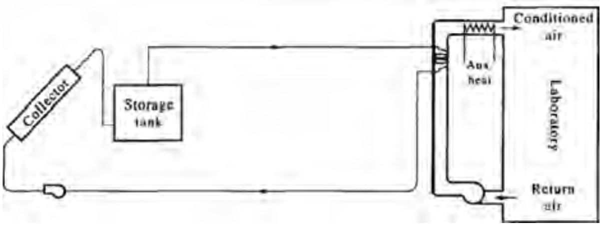

Figure 7 Schematic diagram of the base solar energy system.

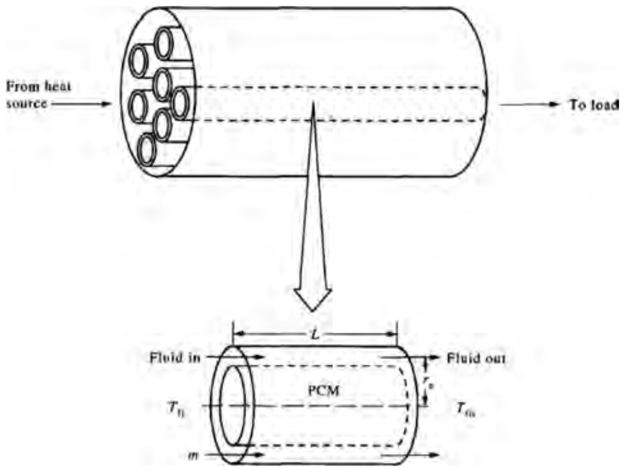

Figure 8 Schematic configuration of latent heat storage tank.

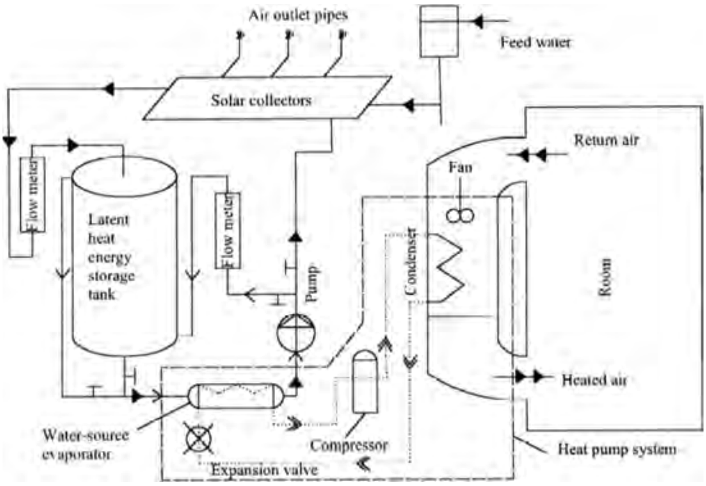

Figure 9 Solar-assisted heat pump system with latent heat storage tank.

collector by the water-circulating pump. When there is low or no solar radiation and the load is not zero during the night and on cloudy days, the cold water from the evaporator is sent to the tank instead of the collector. The cold water extracts heat from the PCM in the tank and it flows to the evaporator for use as a heat source. As a result, at night and cloudy times the stored energy in the tank is used as a heat source for the heat pump. The second mode occurs when solar irradiance is available for collection and the space-heating load is zero. In this mode, the hot water is circulated between the collectors and the tank only. He concluded that shorter and thinner pipes should be used for effective heating operations.

Normally, a solar air heater shows lower efficiency and inadequate storage capabilities. Fath et al. (1995) tried to increase the heat transfer rate and efficiency by replacing the conventional absorbers by a set of one-inch diameter tubes that act both as solar energy absorber and turbulence creator. The designed system is shown in Fig. 10. The tubes of the absorber of the collector were filled using thermal energy storage materials (sensible heat: sand and latent heat: paraffin wax; $Na_2SO_4.10H_2O$). He concluded that using paraffin wax (melting point 50 °C) as the latent heat storage material has the effect of damping out, flattening, and extending the effective period of high absorber and air outlet temperatures, and the effective heat rate. PCMs can maintain the absorbing temperature near the melting point, while the outlet air temperature was maintained almost constant for a long time, which can be useful in the utilization process. Based on a simple transient analysis, an explicit expression for the heater absorber and glass cover temperatures, effective gained heat, outlet air temperature, and the heater efficiency has been developed as a function of time. For the system with built-in PCM, the heat load could be provided for 24 hrs/day, at almost constant temperature. With paraffin wax, the outlet air temperature was maintained 5 °C above the ambient temperature for about 16 h (almost 4 h after sunset). The daily average efficiency, with paraffin wax (melting point 50 °C), is about 63.4% as compared to 59% with sand as the storage material and 38.7% for the conventional flat plate system. He recommended that $Na_2SO_4.10H_2O$ (melting point 32 °C) should be used for lower ambient temperature and solar irradiance.

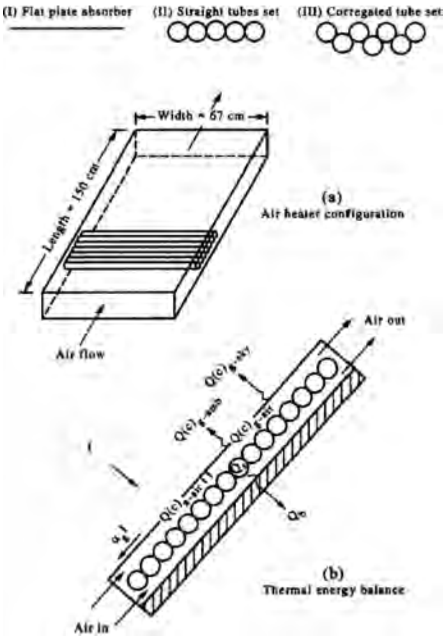

Figure 10 Solar air heater configuration with set of PCM tubes.

A number of researchers have proposed the inclusion of PCMs in walls, partitions, ceilings and floors to serve as temperature regulators. The PCMs have been used to replace masonry in a Trombe Wall. Experimental and theoretical tests have been conducted to investigate the reliability of PCMs as a Trombe Walls (Swet, 1980; Ghoneim et al., 1991). Bourdeau (1980) tested two passive storage collector walls using $CaCl_2.6H_2O$. He concluded that an 8.1 cm PCM wall has slightly better thermal performance than a 40 cm-thick masonry wall. Askew (1978) used a collector panel made of a thin slab of paraffin wax and mounted behind the double-glazing of the building. Collier et al. (1979) showed that a macro-encapsulated PCM material cemented within masonry building blocks results in a significant increase in the system performance over an equivalent volume of concrete. Feldman (1970) studied the feasibility of construction of walls and partitions of cement blocks permeated with stearic acid as a PCM. They measured the storage capacity of these blocks and found it to be higher than cement blocks. Benard et al. (1985) experimentally tested paraffin Trombe Walls with double-glazing. The analysis of the results points out that a controlled air circulation would give good results. Three thermal walls have also been examined using the same test-cell (Benard et al., 1982). This simulation was made with the help of two flat plate air-air heat exchangers totally covering the top and opposite inside walls of the cell. The energy yield of the walls and the temperature variations of the inside room are compared for a 40 cm-thick concrete wall, an 8 cm-thick hard paraffin wall, and an 8-cm thick soft paraffin wall. Trombe Walls using paraffin are one -twelfth smaller than concrete walls and better suited to a retrofit. Strith et al. (2002) used Transparent Insulation Material (TIM) and translucent PCM in the wall for heating the air for the ventilation of the house. Paraffin wax (melting point 25–30 °C, latent heat 150 kJ/kg) was used as a PCM, with 60 kg in a panel with the dimensions of 0.8 × 1.8 × 0.05 m for space heating. The efficiency of solar energy absorbed into the PCM and transferred to the ventilated air was 45% on average. Manz et al. (1997) also carry out the same study with another PCM ($CaCl_2.6H_2O$) as shown in Fig. 11. He proposed a numerical simulation, which fit well with experimental results. He reported that PCMs showed a positive effect and a higher utilization of solar gains can be expected. He also reported that the maximum time ratio parameter could be reached with a mean melting temperature of approximately 20 to 21 °C when the building does not lose energy through the south facing TIM-PCM wall. He recommended further investigation in regard to the practical applications of the system in buildings, aspects of reliability, and durability. Arkar et al. (2002) also designed a solar-assisted ventilation system based on PCM storage. He recommended that paraffin-spherical encapsulations provide homogeneous porous effect in the ventilation duct, which can improve the thermal conductivity of paraffin. He reported that ambient air could be cooled for 3 to 4 K in a clear summer night.

Abhat (1981b) used a modular heat-pipe exchanger concept for use in a latent heat storage system for solar heating applications. The thermal analysis provides the influence of various geometric and thermal parameters on the storage charging time and temperature gradients for heat flow into two markedly different storage substances. Results indicate the capability of the heat exchanger concept to operate within small temperature swings (>10 K) for realistic heat input rates. Comparisons between data and predictions of the test model showed adequate agreement. An active storage system for solar space heating and cooling (Fig.12) was developed (Maccracken, 1981). It consists of a close-spaced plastic tubing mat coiled into a spiral and inserted into a cylindrical tank containing PCM as a heat exchanger. The system contains salt hydrate as a PCM consisting of 98% sodium thiosulphate pentahydrate and two percent sodium sulfate for space heating applications and magnesium chloride hexahydrate for space cooling units. The plastic heat exchanger had the advantage of being low cost and being non-corrosive. 1.27 cm diameter plastic tubing with 2.5 cm spacing takes care of poor thermal conductivity of the PCM. The system was successfully tested for 1000 cycles without any degradation in the performance of the system.

A latent heat solar roof was tested in a Peruvian Village (altitude ≃3000m, latitude ≃13°S) to maintain near isothermal conditions in an experimental chicken brood (Benard et al., 1981). The brooder house was divided into two connecting parts, and a heated enclosure (Fig. 13). Two semi-circular tanks with their upper face closed with glass containing 42 kg of paraffin wax are located below an airtight glass roof. At night, thick polyurethane insulators were placed between the glass roof and paraffin tanks, which helps to regulate the temperature of the enclosure to stay between 22 °C and 30 °C. This temperature is suitable for breeding young chickens with the regularly renewed air.

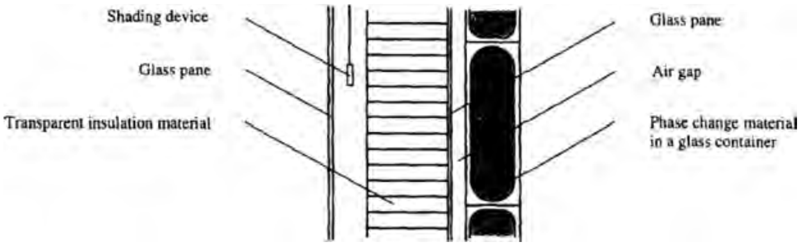

Figure 11 Prototype of TIM - PCM external wall system.

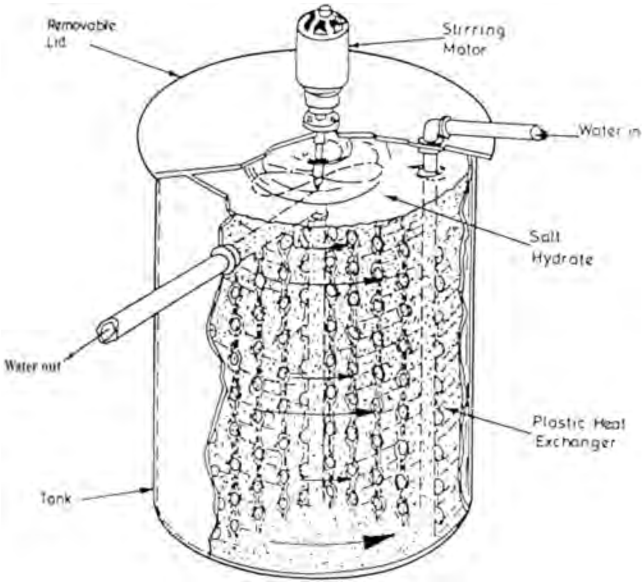

Figure 12 Calmac Corporation – PCM storage device.

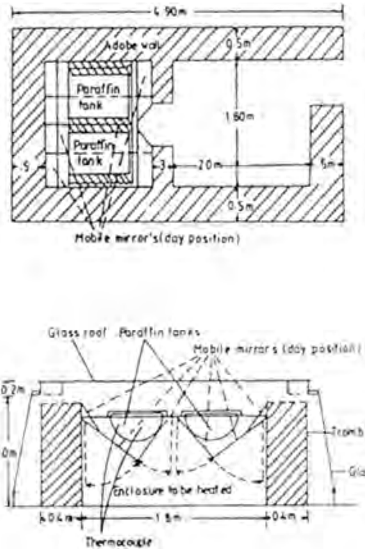

Figure 13 East west vertical cross section of a solar enclosure.

Various systems have been implemented, including an electrical floor heating system in Japan (Shumitomo Chemical, 2004). The most successful PCM thermal energy storage system is a large-scale heat storage system using spherical resin capsules (Mitsubishi Chemicals, 2004). PCM was also extensively used in building materials for passive utilization (Neeper, 2000; Feldman et al., 1995). Nevertheless, PCM takes a longer time to charge or discharge heat because of the thermal resistance of the solid phase on the inner wall. Therefore, direct heat exchange between the PCM and the medium can give higher heat transfer (Inaba et al., 1997b). A method in which micro-capsulated PCM is floated in a heating medium has been proposed (Shibutani, 2002). There are few examples of direct heat exchange with air as a heat transfer medium (Yamaha et al., 2001; Turpenny et al., 2000). A new type of heat storage system based on PCM granules consisting of porous media and paraffin wax has been proposed (Nagano et al., 2004a; Takeda et al., 2004). This system gives a simple mechanism for heat exchange and a high heat transfer coefficient. Numerical results show that the heat transfer coefficient and the proposed non-dimensional time can be used to estimate the amount of exchanged heat and the required time for phase change to be completed for different velocity and temperature conditions.

A theoretical model of a shell-and-tube PCM storage unit was reported (Ismail et al. 1986). The numerical results show the effects of the Biot number, the relative diameters of the tubes, and the inlet fluid temperature on the thermal performance of the unit. Visser (1986) developed a component model for numerical description of two different short-term heat storage vessels. In both vessels, the energy is stored as the latent heat of PCMs. The transient simulation program was used to determine the performance of the cylindrical energy storage tank, which can be used in solar assisted domestic heating by heat pump system. Yimmer and Adami (1989) suggested a numerical model for optimizing a basic one-dimensional, shell-and-tube type thermal energy storage system. Effects of the inner tube, outer shell radii and thermal conductivity of the PCM on the performance of the unit were discussed. A theoretical model to predict the transient behavior of a shell-and-tube latent heat storage unit was presented (Lacroix, 1993a). PCM was put in the shell and heat transfer fluid circulates inside the tubes. Effects of various thermal and geometric parameters on the heat transfer process and on the behavior of the system were confirmed.

Long-term performance of an air based solar heating system using a PCM was estimated (Sagara et al., 1994). Theoretical heat transfer models within PCM spherical capsules were studied. Effect on the overall coefficient of performance (COP) was studied with respect to the capacity of the PCM storage tank, melting temperature, collector area and air flow rate. They reported that the simple uniform temperature model is useful for long-term system simulations. Sari and Kaygusuz (2002) prepared a eutectic (lauric acid 75.5 wt% + stearic acid 24.5 wt%) with melting point at 37 °C and latent heat of 183 kJ/kg for passive solar space heating applications, such as building and greenhouse heating with respect to the climate conditions. Eutectic encapsulated in the annulus of two concentric pipes shows good heat transfer characteristics, and it has potential for heat storage in passive solar space heating systems.

A computer model was developed for space heating and cooling applications (Vakilaltojjar et al., 2001). The effect of PCM slab thickness and fluid passage gap on the storage performance was investigated. The author put the PCMs ($CaCl_2.6H_2O$ and $KF.4H_2O$) in thin flat containers and air is passed through gaps between them. He concluded that the air velocity profile at the entrance does not affect the heat transfer characteristics and the outlet air temperature considerably. Using smaller air gaps and thinner PCM slabs can obtain better performance, however, this increases the number of PCM containers and the total volume of the storage system which will lead to higher-pressure drop across the storage system.

Several efforts have been made to develop PCM storage systems to utilize off peak electricity (Shitzer et al., 1983; Farid et al., 1990; Hatano et al., 1995; Lin et al., 2004). Using off peak electricity, PCM can melt to store electrical energy in the form of latent heat. Stored heat could utilize the peak period of electricity. Therefore, if latent heat storage systems are coupled with the active systems, it can help to reduce the peak load. Lin et al. (2004) analyzed the thermal performance of a room with an under-floor electric heating system with shape-stabilized PCM plates. This system can be used in various climates and will help to design such kinds of under-floor electric heating systems. Farid et al. (1990) used paraffin wax (55 °C) encapsulated in a thin metal container to replace the ceramic bricks. An electrical plate heater was fixed at the axis of each storage unit to provide low heat flux but sufficient to melt all the wax. During charging, PCM stores latent heat of melting, which is continuously discharged during the other periods. An electrical plate heater was fixed at the axis of each storage unit to provide low heat flux but sufficient to melt all the wax within 8 h. They concluded that latent heat storage systems could shift the peak-heating load. A floor heating system with Na_2SO_4 .$10H_2O$ as a PCM was used for heating using off-peak electricity in Japan (Hatano et al., 1995).

Space Cooling

The most common storage media for space cooling are water, ice, and PCM, commonly known as eutectic salts. Ice has been used as a commercial PCM for years. Various technologies have been developed for ice storage. Some selected technologies for low temperature applications are: ice harvesting storage systems, external melt ice-on-coil storage systems, internal melt ice-on-coil storage systems and encapsulated ice. Normally, internal melt ice-on-coil systems and encapsulated ice systems use standard packaged chillers that have been configured to chill secondary coolants to ice-making temperatures. External melt systems may be installed with packaged chillers or with site assembled refrigeration plants. Ice harvesters use packaged or site assembled refrigeration systems (Dorgan, 1993).

PCMs have been used for various heat storage applications since the 1800s, but they have only recently been used as a storage media for space cooling. So far, most of the PCMs for cool storage are inorganic salt hydrates, organic paraffin waxes, and mixtures of these. A theoretical simulation of cool storage was reported (Solomar et al., 1989; BoHe et al., 2001). BoHe et al. investigated the potential for using cool storage systems using PCMs, and static and dynamic cool storage processes are discussed. They reported that the Rubitherm RT5 (melting point 7 °C, latent heat of fusion 158.3 kJ/kg) appears to be an excellent candidate as a PCM for cool storage because of its economical cost, congruent melting, self-nucleation property, lack of super-cooling, and stability during a number of cooling and heating cycles. They concluded that the volume contraction of the phase change process should not be neglected in a cooling storage system. If sufficient heat transfer area is available (e.g., floor or plant heat exchanger), the static storage system can be used. In the dynamic storage system, direct contact between the storage material and the heat transfer medium results in excellent heat transfer.

Identification of commercial PCMs for cool storage at 15–23 °C was carried out (Chemical Industry Report, 1988). Thermal characteristics of manganese (II) nitrate hexahydrate (melting point 25.8 °C, latent heat of fusion 125.9 kJ/kg) as a PCM was examined for cooling applications (Nagano et al. 2003). They presented a general procedure for mixing and examination of PCMs for latent heat storage. They reported that almost all chlorides were effective in modulating the melting point of $Mn(NO_3)_2.6H_2O$. $MnCl_2$.$4H_2O$ was an effective additive with respect to modulation of melting point, reduction of super-cooling and quantity of the heat of fusion. The indoor air at temperature of 28 °C in daytime and the outside cool air at night below 16 °C can be utilized to melt and solidify this mixture.

Latent heat storage systems have been studied for air conditioning (Telkes, 1974; Gaorvon et al., 1977; Herrick, 1978). Inorganic hydrous salts have been used as storage material. Lane (1975) also suggested some PCMs for cooling and dehumidification. Farid et al. (1988) studied the feasibility of cool storage using dimethyl sulfoxide (melting point 16.5 °C) as a PCM in a rectangular container. Based on the experimental results and the model predictions, dimethyl sulfoxide can be used as a PCM for cool storage. The results also show that, cooling extraction period depends on the amount of solidified PCM. The cool extraction period was completed when the outlet air temperature from the PCM section reached at 25 °C. This temperature is considered the highest temperature at which the human may feel comfortable. An experimental and theoretical study was conducted for an encapsulated thermal storage tank (Saitoh and Hirose, 1986). They used $Na_2HPO_4.12H_2O$ as PCM to fill cylindrical capsules with an inside diameter of 70.7 mm. They concluded that the main factors affecting the charging process were the capsule material, size, coolant flow rate and temperature. Kondepudi et al. (1988) also discussed the effect of Biot number, Stefan number, and Fourier number on the thermal performance of cold storage. Laybourn (1988) utilized a concept of thermal resistance, which embraced the convective resistance, wall resistance, and ice layer resistance to calculate the cold storage of the tank with rectangular capsules. Arnold (1990) analyzed the heat transfer during the freezing and melting process by performing a series of charging and discharging experiments. Chen et al. (1991a; 1991b; 1991c) developed a general lump model to predict the thermal performance of a cold storage system. The results showed that the lump model is a convenient and simple method to determine the thermal performance of a cold storage system. Ryu et al. (1991) used a rectangular storage tank with a copper tube container and conducted a series of experiments using both vertical and horizontal tank configurations to investigate heat transfer characteristics. Chen et al. (1991d) conducted a series of experiments to investigate the sub-cooling phenomenon and the freezing probability of water with and without nucleation agents inside a cylinder. They verified that the addition of nucleation agents is one of the approaches to improve the sub-cooling phenomenon effectively. Chen et al. (2000) experimentally investigated the pressure drop of an encapsulated thermal storage tank during the charging process. The cylindrical capsules inside the thermal storage tank utilize water with nucleation agents added as PCM, and the coolant is the aqueous solution of ethylene glycol. The results indicate that cool energy can be fully stored in the form of latent heat when the inlet coolant temperature is set below the temperature with 100% nucleation probability. They concluded that high cold storage could be obtained by using the lower inlet coolant temperature with high flow rate. The heat transfer coefficient increases as the coolant flow rate increases. The pressure drop flowing through tank is enlarged as the coolant flow rate increases during the charging process.

Greenhouse Heating

Solar agricultural greenhouses have been widely used in the past two decades in order to increase plant quality and productivity and to reduce consumption of fossil fuels for heating and cooling. The most effective greenhouses require control of temperature, humidity, solar irradiance and internal gas composition with rational consumption of energy (Boulard et al., 1990; Santamouris et al., 1994; Merritt et al., 1995; Marinkovi et al., 1998; Kurklu, 1998). Research work in this area, involving studies of new materials, heat storage and heat exchange devices resulted in some interesting demonstration units followed by rapid commercial applications. The most frequently used PCM for these purposes are $CaC1_2.6H_2O$, $Na_2SO_4.10H_2O$, PEG, and paraffins (Kurklu, 1998).

Kurklu (1998) has summarized work on greenhouses using PCM. $CaC1_2.6H_2O$ and $Na_2SO_4.10H_2O$ have been widely used because of low cost and high heat storage capacity with suitable melting point, but super-cooling and sensitivity towards moisture are serious disadvantages for long-term use. Nishina and Takakura (1984) used $Na_2SO_4.10H_20$ with some additives to prevent phase separation and degradation for heating a greenhouse in Japan. Fig. 14 shows the general view of the experimental set-up. They concluded that 40 - 60% of the latent heat potential of the PCM was realized, which indicated that almost half of the PCM was not used efficiently during the energy exchange processes. Takakura et al. (1981) tested polyethylene glycol and $CaCl_2.6H_2O$ as PCMs in greenhouse heating for 7.2 m^2 ground area. They compared conventional greenhouses with PCM storage type greenhouses. The efficiency of the greenhouse with PCM storage integrated with solar collector was 59% and able to maintain 8°C inside the greenhouse at night, when the outside temperature dropped to –0.6 °C. A microcomputer control system has been developed in order to establish more accurate and more sophisticated control for solar greenhouse systems.

CNRE-France conducted a study for rose production in a 500 m^2 single glazed greenhouse by utilizing 13.5 tons of $CaC1_2.6H_20$ (melting at 28°C) (Jaffrin and Cadier, 1982; 1987). Fig. 15 shows the arrangement of the PCM containers underground. The solar heat available inside the greenhouse was transferred and stored by recycling the air through an underground of flat heat exchangers filled with a PCM. The performance of the PCM greenhouse was compared with a traditional greenhouse of identical geometry having the same plantation. The PCM greenhouse achieved an 80% savings in propane gas as compared with the traditional greenhouse to maintain the same temperature. Latent heat

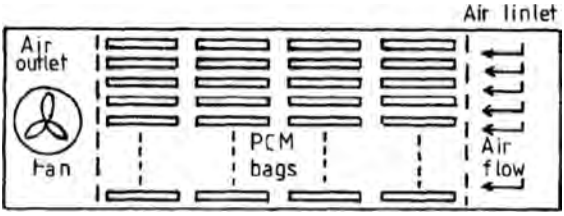

Figure 14 General view of phase change energy storage system.

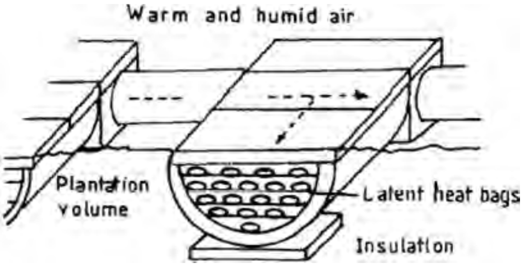

Figure 15 Underground tunnel: equipped with a PCM.

storage materials can also be stacked in racks placed in a greenhouse (Fig. 16), which will be directly heated by the solar radiation (Song, 1988). In this system, the hot air was circulated in the greenhouse through the storage to increase the rate of charging/discharging of PCM. The stored heat was utilized during off sunshine hours to maintain the desired temperature of the greenhouse. $Na_2SO_4.10H_2O$ was used as PCM storage material in the greenhouse. Hung et al. (1975; 1983) had designed and constructed a latent heat storage system with two different stacking configurations and air baffling as an integrated part of the greenhouse solar system. Commercial cylindrical storage rods were used as the primary storage elements. The results showed that the designed latent storage systems demonstrated significantly higher compact storage capacity than the rock or water storage. It is revealed that the ring-baffled storage unit performed better than the cross-baffled storage unit.

Levav and Zamir (1987) tested $CaC1_2.6H_20$ in greenhouses and reported that required air temperature in the greenhouse was achieved without any increase in the relative humidity. It was stressed that the most important drawback of the system was the high cost of the PCM. Furthermore, they indicated that the 24°C melting temperature of the PCM could be high for some crops. Kern et al. (1979) used $CaC1_2.6H_20$ as a PCM in aerosol cans to investigate heat storage possibilities both inside and outside in a 36 m^2 ground area greenhouse covered with fiberglass. They reported that phase change storage system can provide a desirable alternative to rock storage. Paraffins have also been used for energy storage in greenhouses. A study performed by Bagetinelik et al. (1994) was the only work in the literature using paraffin (melting point 48–60 °C , latent heat of fusion 190 kJ/kg) for greenhouse heating.

Recently, Kfirklti et al. (1996; 1997) used $Na_2SO_4.10H_20$ as a PCM in greenhouses. In their study, two types of a similar PCM, one with a melting range of 22–25°C and the other with one about 8°C, were employed, the former for the reduction of peak temperatures towards summer and the latter for frost prevention in greenhouses. Fig. 17 shows an experimental set-up of energy storage used in a greenhouse. They concluded that solar collection efficiency with PCMs was 29% (at 22–25°C) and 30% (at 8°C) respectively. They suggested that PCMs could be used for both energy storage and humidity control in greenhouses. This helps manage energy effectively in greenhouses.

Enibe et al. (2002; 2003) designed, constructed and performed an evaluation of a natural circulation solar heating system using PCM energy storage. The system consists of

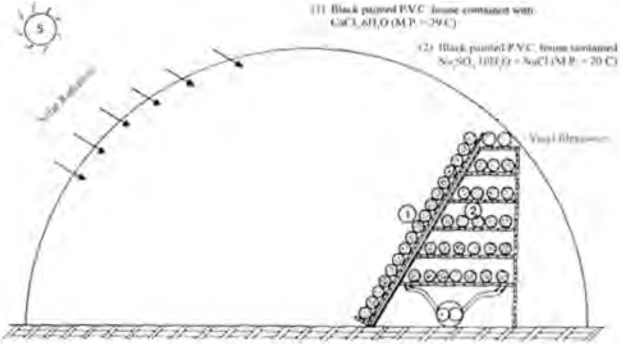

Figure 16 Greenhouse with PCM stacked in racks.

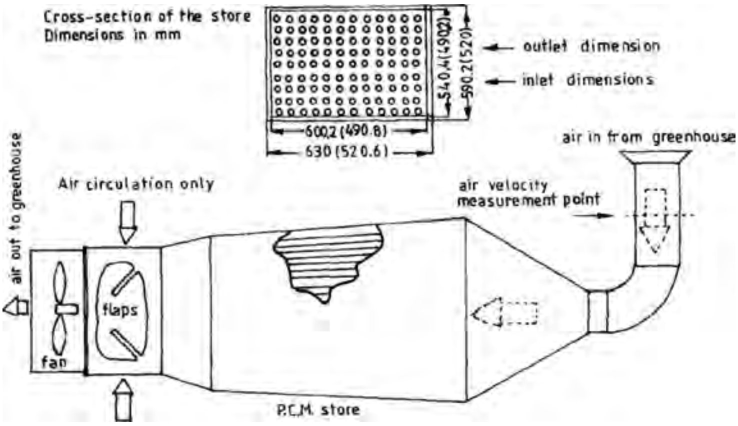

Figure 17 General view of the storage used for energy management in greenhouse.

a flat plate solar collector integrated with paraffin PCM for energy storage. The PCM is prepared in modules of thin rectangular blocks of PCM encapsulated by the rectangular walls of a box-like structure, which behaves like thin fins. The encapsulating box is made of a material of good thermal conductivity, and divided into a number of compartments of identical dimensions. A number of such modules are equally spaced across the collector, as shown in Fig. 18 a & Fig. 18 b. The space between each module pair serves as an air heater, the heaters being connected to common air inlets and discharge header manifolds. By natural convection, ambient air enters the inlet header through control valve A, while heated air leaves the discharge header through valve B, flows into the hot air chamber, and is discharged to the environment through valve C. They concluded that the peak temperature rise of the heated air was about 15 K. The collective useful efficiency was about 50%. This system is suitable for use as a solar cabinet crop dryer for aromatic herbs, medicinal plants and other crops, which do not require direct exposure to sunlight.

Solar cooking

Solar cookers are used to cook rice, vegetables, meat, bake cakes, etc. The detailed design, testing, theory, and utility of box-type solar cookers are well developed (Telkes, 1959; Abhat 1981a; Mullick et al., 1987; Thulasi et al., 1994; Buddhi et al., 2000). The use of these solar cookers is limited because they do not have any storage, i.e., these cookers cannot be used on cloudy days or in the late evening. PCMs can be used for storing the solar heat in the form of latent heat in daytime; after that, stored heat can be used for evening / night cooking or on cloudy days (Domanski et al., 1995; Buddhi and Sahoo, 1997; Sharma et al., 2000; Buddhi and Sharma, 2003). A box-type solar cooker with PCM was designed and fabricated for the composite climatic conditions of India (Buddhi and Sahoo, 1997). Commercial-grade stearic acid (melting point 55 °C, latent heat of fusion 161 kJ/kg) was used as a PCM.

Fig. 19 shows the sketch of a box-type solar cooker for one vessel using a PCM to store the solar energy. In the center of the absorbing plate 'A,' a cylindrical container of

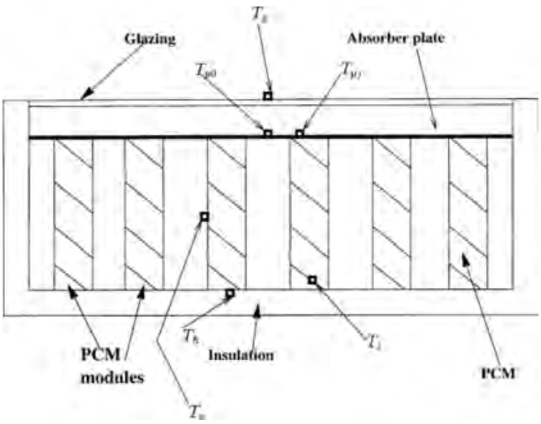

Figure 18a Cross-section view of collector assembly with PCM.

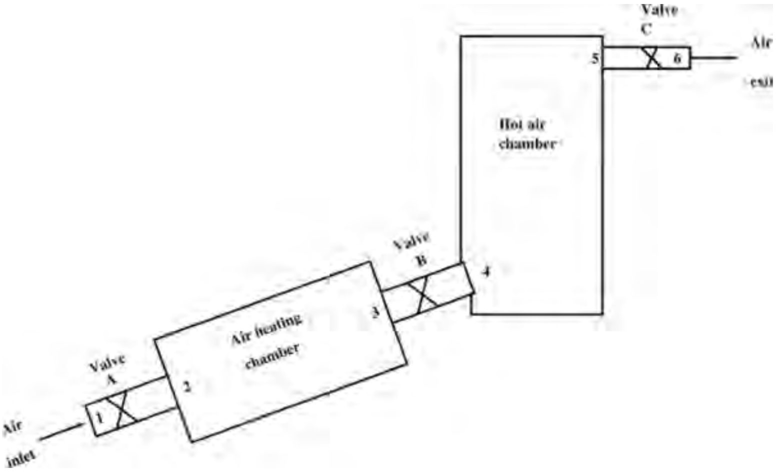

Figure 18b Schematic diagram of natural circulation air heater with PCM.

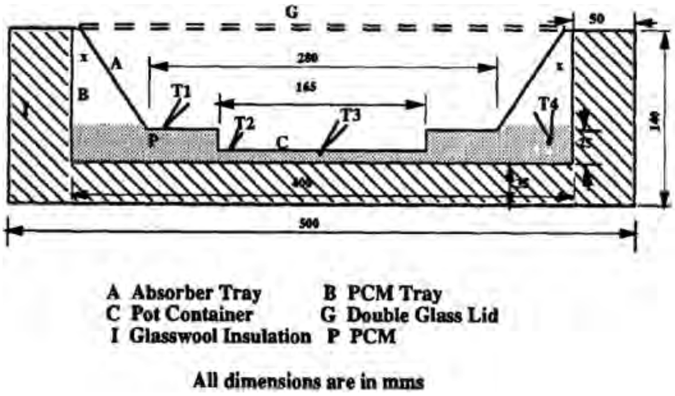

Figure 19 Schematic diagram of the box of a solar cooker with PCM storage.

0.165 m diameter and 0.02 m in depth was welded (shown in Fig. 18 by ‘C’), and the cooking pot is to be kept tightly in it. This container will provide a heat transfer from the absorbing plate and PCM. Moreover, aluminum fins were also provided at the inner side of the tray and cylindrical container. The outer tray ‘B’ is also made from the same aluminum sheet. The distance between tray ‘A’ and tray ‘B’ was kept at 0.025 m on the bottom side. Tray ‘B’ was filled with 3.5 kg of commercial grade stearic acid (PCM) and it was made sure that the PCM was in good contact with the bottom side of tray ‘A.’ The space between tray ‘B’ and the casing was filled with glass wool to provide thermal insulation to the bottom and sides of the solar cooker. A flat glass mirror was fixed in an aluminum cover to serve as a booster and as a cover for the glass lid when the cooker is not exposed to solar radiation. The aluminum tray ‘A,’ cooking pot and its cover were painted with a dull black paint on the outside.The experimental results demonstrate the feasibility of using a PCM as the storage medium in solar cookers, i.e., it is possible to cook the food even in the evening with a solar cooker having latent heat storage. It also provides a nearly constant plate temperature in the late evening.

Domanski et al. (1995) investigated the possibility of cooking during non-sunshine hours using PCM. They designed the storage-cooking vessel for non-sunshine hours (Fig. 20). For this purpose, two concentric cylindrical vessels (0.0015 m thick), made from aluminum, are connected together at their tops using four screws to form a double-wall vessel with a gap between the outer and inner walls. The outer and inner vessel have a diameter of 0.18 m and 0.14 m. The annular gap between the outer and inner vessels is 0.02 m. This gap is covered with a removable aluminum cover into which three circular holes were drilled to allow inserting of thermocouples and permit direct visualization during filling or removing of the PCMs. A circular aluminum cover is used as the lid for the inner vessel. The gap between the outer and inner vessels was filled with 1.1 kg of stearic acid (69 °C), or 2.0 kg of magnesium nitrate hexahydrate (89 °C), which leaves sufficient space for expansion of the PCMs on melting. Cooker performance was evaluated in terms of charging and discharging times of the PCMs under different conditions. They reported that performance depends on the solar irradiance, mass of the cooking medium, and the thermo physical properties of the PCM. The overall efficiency of the cooker during discharging was found to be 3-4 times greater than that for steam and heat-pipe solar cookers, which can be used for indoor cooking. In such a type of design, the rate of heat transfer

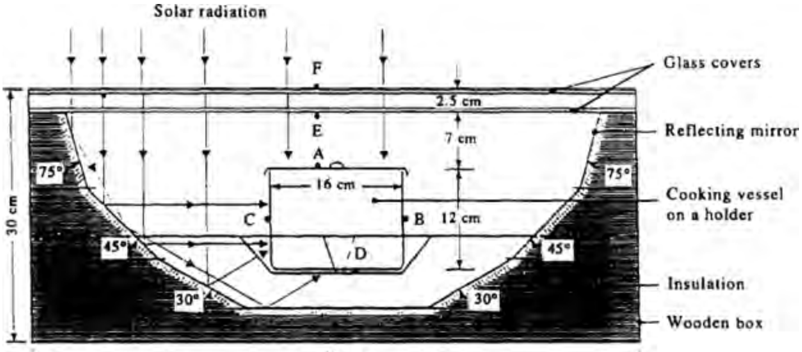

Figure 20 Solar cooker with PCM cooking container.

from the PCM to the cooking pot is slow, and more time is required for cooking the evening meal.

Sharma et al. (2000) designed and developed a cylindrical PCM storage unit for a box-type solar cooker to cook the food in the late evening. Because this unit surrounds the cooking vessel, the rate of heat transfer between the PCM and the food is higher, and cooking can be faster. For this purpose, a PCM container to hold the cooking vessel was designed and fabricated as shown in Fig. 21. It has two hollow concentric aluminum cylinders of diameters 18 cm and 25 cm, and is 8 cm deep with a 2 mm thickness. The space between the cylinders was filled with acetamide (melting point 82 °C, latent heat of fusion 263 kJ/kg) as a PCM. The dimensions of the vessel used for cooking were 17.5 cm and 10 cm in diameter and height, respectively, and it can be inserted inside the PCM container for cooking purposes. To enhance the rate of heat transfer between the PCM and the inner wall of the PCM container, eight fins (1x3 cm) were welded at the inner wall of the PCM container. They reported that by using 2.0 kg of acetamide as a latent heat storage material, the second batch of food could be cooked if it is loaded before 3:30 P.M. during the winter season. They recommended that the melting temperature of a PCM should be between 105 and 110 °C for evening cooking. Therefore, there was a need to identify a storage material with appropriate melting point and quantity, which can cook the food in the late evening. To store a larger quantity of heat in a PCM, more input solar radiation would be required. Hence, Buddhi and Sharma (2003) used a latent heat storage unit for a box type solar cooker with three reflectors. They used acetanilide (melting point 118 °C, latent heat of fusion 222 kJ/kg) as a PCM for night cooking. To conduct the cooking experiments with the PCM storage unit, a double glazed (glass covers) box-type solar cooker having a 50 cm × 50 cm aperture area and being 19 cm deep was used. In this solar cooker, three reflectors were provided, i.e., the middle reflector was mounted with a hinge and had rotation only about the horizontal axis. The other two reflectors were fixed by a ball and socket mechanism in the left and right sides of the reflector. This pair of reflectors has three degrees of freedom, i.e., they can have movement about the horizontal axis, and vertical axis and can rotate about both the axes. By these mechanisms, efforts were made to keep the reflected solar irradiance on the absorber surface to enhance the incident solar radiation on the glass cover during the course of the sun exposure experiments.

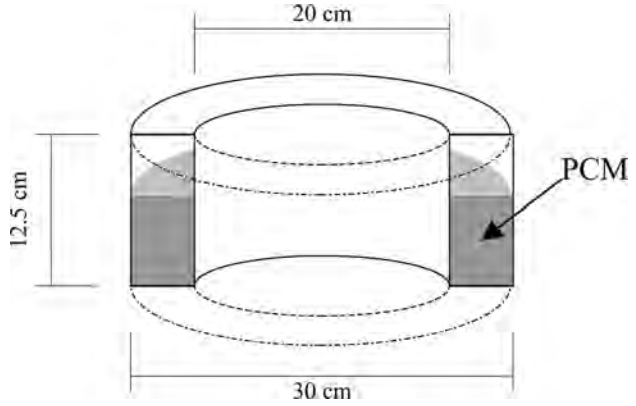

Figure 21 A schematic diagram of the latent heat storage unit.

Following Sharma et al. (2000), a cooking vessel with latent heat storage was designed and fabricated to cook the food in night. The unit has two hollow concentric aluminum cylinders of diameter 20 and 30 cm, and is 12.5 cm deep and 2 mm thick. The space between the cylinders was filled with 4.0 kg of PCM to conduct the cooking experiments with all three reflectors. The dimensions of the vessel used for cooking were 19 and 15 cm in diameter and height, respectively, and it can be inserted inside the PCM storage unit for cooking purposes. To enhance the rate of heat transfer between the PCM and the inner wall of the PCM container, eight fins (1 cm × 3 cm) were welded at the inner wall of the PCM container. From the experimental results, one can conclude that the cooking experiments were successfully conducted for the evening time, cooking up to 8 P.M. with 4.0 kg of PCM during winter season in India.

Sharma et al. (2004) developed a solar cooker based on Evacuated Tube Solar Collector (ETSC) with PCM storage, as shown in Fig. 22. It consists of an ETSC, a closed loop pumping line-containing water as Heat Transfer Fluid (HTF), a PCM storage unit, cooking unit, pump, relief valve, flow meter, and a stainless steel tubing heat exchanger. The PCM storage unit has two hollow concentric aluminum cylinders, and its inner and outer diameters are 304 mm and 441 mm, respectively, and is 420 mm deep and 9 mm thick (Fig. 23). The space between the cylinders was filled with 45 kg erythritol (melting point 118 °C, latent heat of fusion 339.8 kJ/kg) used as the PCM. A pump circulates the heated water (HTF) from the ETSC through the insulated pipes to the PCM storage unit by using a stainless steel tubing heat exchanger that wraps around the cooking unit by closed loop. During sunshine hours, heated water transfers its heat to the PCM and is stored in the form of latent heat through a stainless steel tubing heat exchanger. This stored heat is

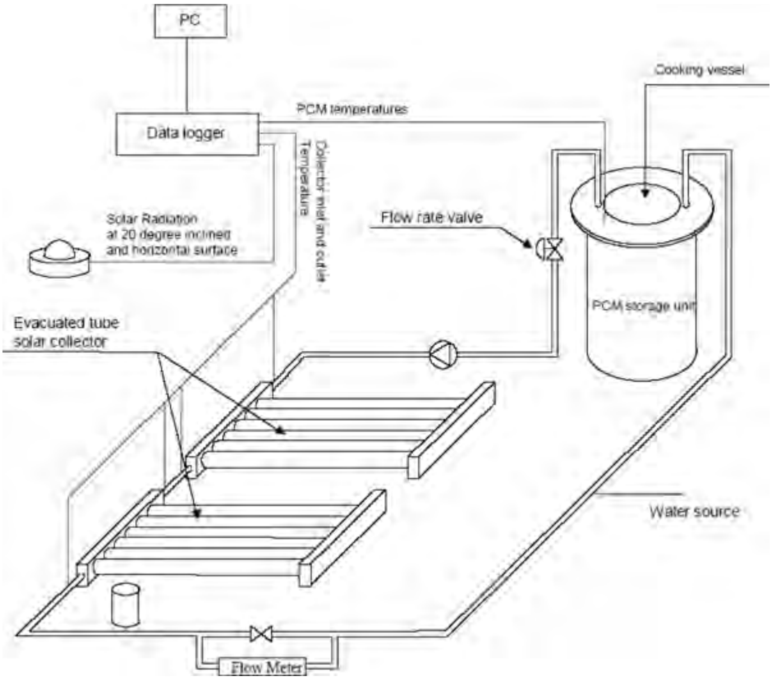

Figure 22 Outline of the prototype solar cooker based on evacuated tube solar collector with PCM storage unit.

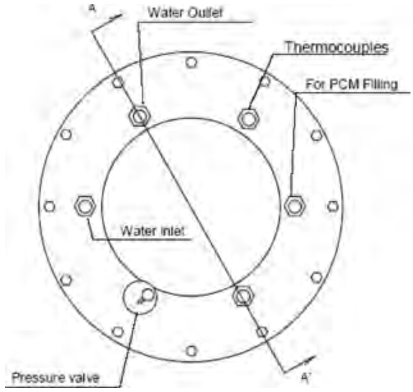

Figure 23a Verticalview of the PCM storage unit.

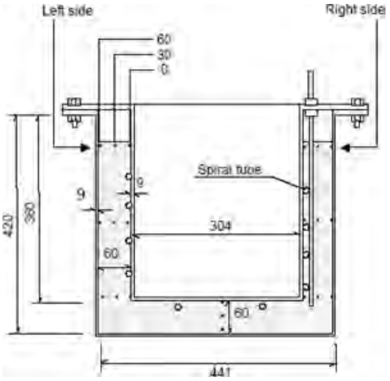

Figure 23b Verticalview of the PCM storage unit.

utilized to cook the food in the evening time or when sun intensity is not sufficient to cook the food. They concluded that two cooking times (noon and evening) were in a day. Noon cooking did not affect the cooking in evening, and evening cooking using PCM storage was found to be faster than noon cooking. Experiments and analysis indicated that the prototype solar cooker yielded satisfactory performance in spite of low heat transfer; the modified design of heat exchanger in the thermal storage unit will enhance the rate of heat transfer in the present set-up.

Ramadan et al. (1987) designed a simple flat-plate solar cooker with focusing plane mirrors using energy storage materials. In his design, a jacket of sand (1/2 cm thick) around the cooking pot has improved the cooker performance tremendously. They concluded that six hours per day of cooking time have been recorded. Approximately three hours per day of indoor cooking has been achieved. Overall energy conversion efficiency up to 28.4% has been obtained. The possibility of using a PCM as a storage medium to obtain longer cooking periods was studied. A thin layer of the salt hydrate $Ba(OH)_2{\cdot}8H_2O$ as a jacket around the cooking pot was suggested. Bushnell (1988) presented a prototype for solar ovens, which employ pentacrythritol as a solid-solid PCM. He described the performance from efficiency measurements and determination of figure of merit.

Waste Heat Recovery Systems

Air conditioning system eject (sensible and latent) heat, in which sensible heat accounts for about 15–20% of the total exhausting heat (Zhang, 1999). The exhausting temperature of the compressor is relatively high (<65 °C) when using Freon as refrigerant. Therefore, it can be recovered using an accumulator and gets heat of higher temperature. Gu et al. (2004) developed a heat recovery system using PCM to recover the rejected heat of air conditioning systems and produce low temperature hot water for washing and bathing. They concluded that the heat recovery system decreases not only the consumption of primary energy for heating domestic hot water but also the calefaction to the surroundings due to the rejection of heat from air conditioning systems. It was observed that the efficiency ratio of the system is improved effectively when all the rejected (sensible and latent) heat from air conditioning systems is recovered. The technical grade paraffin wax and the mixtures with liquid paraffin and lauric acid qualify as PCM for heat recovery of air conditioning systems.

An effective utilization of urban waste heat from co-generation systems is typically available at temperatures of 60–100 °C. Ona et al. (2001) have investigated erythritol (melting point 118 °C; latent heat of fusion 339.8 kJ/kg) that can be used for relatively high temperature industrial waste heat processes. Several studies have been done on stearic acid (Buddhi and Sharma, 1999; Sari and Kaygusuz, 2001). This material has a melting point between 60–70 °C and is expensive. It has only been found to be of limited use in waste heat systems. Nagano et al. (2004b) proposed a mixture of $Mg(NO_3)_2.6H_2O$ as a base material with $MgCl_2 \cdot 6H_2O$ as an additive to modulate the melting point. They reported that the addition of 5–10 wt% of $MgCl_2 \cdot 6H_2O$ can set the $Mg(NO_3)_2.6H_2O$ (melting point 80 °C, latent heat of fusion 150 kJ/kg). Increasing the mix ratio had little effect on heat of fusion, but allowed the melting point to be reduced to about 60 °C. No degradation in the melting point and latent heat of fusion were observed after 1000 accelerated thermal cycles.

Yagi et al (1995) conducted a fundamental study on heat transfer for developing a heat storage process by latent heat for recovering high temperature waste heat over 500 K. Heat transfer experiments were attempted for a single encapsulated phase change material and for a packed bed. The metal PCMs were found to be excellent for heat storage because of uniform temperature in the capsule. Simulation results show that the concurrent flow for heat storage and release showed better results for effective use of storage heat than counter-current flow.

Buddhi (1997) designed and fabricated a shell and tube type heat exchanger for low temperature waste heat recovery using PCM (Fig. 24). Stearic acid (59 °C, 198 kJ/kg) was used as a PCM for this study. To enhance the effective thermal conductivity of the system, the radial distance between the tubes was kept at 3 to 4 cm. The shell was filled with 50 kg commercial grade stearic acid. Hot and cold water was used as a Heat Transfer Fluid (HTF) for charging / discharging of the PCM. Ambient temperature, flow rate and PCM temperatures were measured simultaneously at an interval of 15 minutes. He concluded that the experimental results show the feasibility of using PCM as storage media in heat recovery systems. Due to poor thermal conductivity of the PCM the overall heat transfer coefficient is quite low and fins should be provided to increase the effectiveness of the

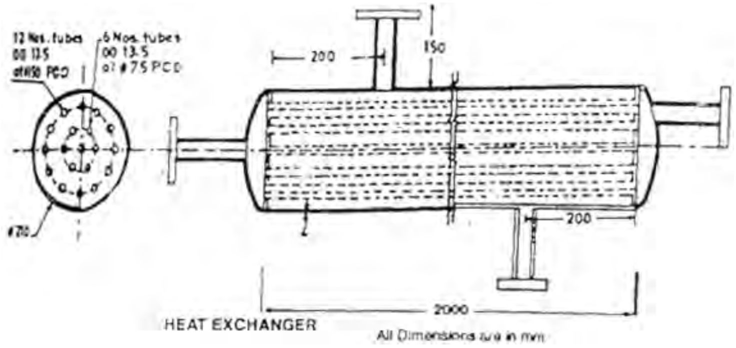

Figure 24 Shell and tube type heat exchanger with latent heat storage material.

heat exchanger. Distance between tubes, fins, and mass flow rates should be selected carefully in order to optimize the performance of the heat exchanger. Paraffin wax (54 °C, 184 kJ/kg) was also used in a shell and tube type heat exchanger for waste heat recovery (Buddhi, 2003). Fins were also used for effective heat transfer.

LATENT HEAT STORAGE EXCHANGER

Latent heat storage systems mainly depend on PCM investigations and on the development of heat exchangers that assure a high effective heat transfer rate to allow rapid charging and discharging. Heat exchangers with a high temperature PCM not only have a high capacity to store thermal energy, but also can make the stored energy be highly applicable. It is always a problem to get a sufficient rate of heat transfer from the latent thermal energy storage systems due to poor performance of heat exchangers. So far, some different types of heat exchangers have been developed to overcome this shortage.

Double pipe heat exchangers for latent heat storage have been studied (Fath, 1991). This research suggested that increasing the air inlet temperature, air mass flow rate, and heat exchanger length could enhance heat transfer rate. Single full-length heat exchangers exhibited better thermal effectiveness than two half-length and equal capacity parallel heat exchangers. A direct contact heat exchanger with an immiscible heat transfer fluid moving in the PCM has eliminated the permanent heat exchange surface and has been confirmed to prevent phase separation of the PCM (Farid et al., 1989). Classical double-pipe or shell-and-tube heat exchangers have been applied in the storage energy systems and a relevant theoretical and experimental analysis of the phase-change phenomenon has been restricted to geometry of a cylindrical capsule (Domanski et al., 1994), an annulus gap, spherical or rectangular enclosures (Dietz, 1984). Another novel configuration includes the use of three types of PCMs with different melting temperatures (Watanbe et al., 1993). This allows improvement in charging / discharging rates by use of three-type PCMs. Use of plate heat exchangers was thought to provide more efficient and compact heat exchange configuration (Bansal and Buddhi, 1992b). Erk and Dudukovic (1996) presented a novel energy storage system consisting of n-octadecane retained by capillary forces in a porous silica support. This configuration eliminates the expensive heat exchange surface, provides higher energy density, and gives higher rates of energy storage and release.

Lecomte et al (1985) presented a design method for sizing a shell-and-tube latent heat exchanger for a thermal system under thermodynamic conditions. They concluded that high flow rates could not deliver significant heat from PCM to the load. Discharging of heat from PCM to the load depends on the performance of the heat exchanger and thermophysical properties of the PCM. Bathelt and Viskanta (1980) studied the heat transfer during melting from a horizontal cylindrical heat source with a uniform surface heat flux and a uniform surface temperature by circulating a fluid through a multipass heat exchanger embedded in n-heptadecane and n-octadecane. The instantaneous shape of the melt volume was recorded photographically and local heat transfer coefficients at the solid-liquid interface were determined. For quasi-steady melting, the local and average heat transfer is correlated in dimensionless form. Using the correlation, the solid-liquid interface position was calculated and found to be in good agreement with experimental data.

Saxena et al. (1982) presented a preliminary model for estimating possible thermal energy storage in shell-and-tube heat exchangers. Effects of various parameters such as thermal and physical properties of PCM and convective fluid, heat exchanger dimensions and heat transfer fluid flow rates both in laminar and turbulent regime on energy storage times have been discussed. El - Kassaby et al. (1993) simulated the behavior of a low-temperature PCM in a heat exchanger for short-term storage. An excellent agreement was obtained for the outlet air temperature when compared with the experimental measurements, and differences did not exceed 0.5°C over the simulated period. This simulation approach can be used for any PCM with known thermophysical properties and is able to predict the transient moving front for freezing or melting, mass fraction of either liquid or solid phase to the total PCM mass.

Kamimoto et al. (1986a) developed a latent heat thermal storage exchanger using form-stable high-density polyethylene. In their design, the hot fluid entered into the exchanger from the top end during the charging process, whilst cold fluid entered into the exchanger from the bottom end during the discharging process. No explanation was given as to why such an operation mode was adopted. Bellecci et al. (1993) numerically simulated the cyclic thermal processes in a shell-and-tube latent heat thermal storage exchanger. In their design the hot and cold fluids were introduced from the same end of the storage exchanger for the successive charge and discharge processes. Gong et al. (1997) tried to find which operation mode was better between Kamimoto (1986a) and Bellecci et al. (1993). They developed a finite element model to simulate the cyclic thermal process occurring in a shell-and-tube latent heat thermal storage exchanger. This exchanger consists of a tube, which is surrounded by an external coaxial cylinder made up of a PCM. A heat-transfer fluid flows through the tube to store or extract thermal energy from the PCM. Numerical experiments indicated that introducing the hot and cold fluid from the same end of the storage exchanger is more desirable than introducing the hot and cold fluid from different ends of the storage exchanger. Numerical results also provide the guidance for selection of the appropriate mode. The results are limited to only conduction-controlled melting/freezing heat transfer in the PCM.

Hasan (1994) developed a simple tube-in-tube heat exchanger for thermal energy storage with stearic acid as a PCM. He found that the melting front moves in the radial direction inward as well as in the axial direction from the top toward the bottom of the PCM tube. Melting front speed was enhanced by a convection heat transfer mechanism in the melted PCM. Phase transition can also be made faster by placing the heat exchanger in a horizontal position rather than a vertical one. He et al. (2001) presented a theoretical analysis and experimental tests on a novel shell-and-tube latent heat exchanger, which provides a basis for optimal design and operation of the heat exchanger. They reported that some parameters, such as the inlet temperature, the velocity of fluid, the thickness of the PCM and the length of the flow channel have visible effects on the heat transfer performance of the unit. Stable heat output can be obtained by increasing the entrance temperature of heat transfer fluid, PCM thickness, and flow channel length.

Banaszek et al. (1999) used a spiral heat exchanger in latent heat storage unit. Compactness, enhanced heat transfer due to centrifugal forces, easy sealing, large heat transfer surface, and a shorter undisturbed flow length are the most appealing features of this system. Qarnia et al. (2001) presented a mathematical model for simulating the thermal behavior of a cross-flow heat exchanger with layers of PCM sandwiched between the hot and cold air streams to prevent frosting. The mathematical model was validated with experimental data. It was found that thermal resistance affects the exchanger performance by reducing the dimensionless outlet temperature of the cold air stream.

MEASUREMENT TECHNIQUES OF THERMO-PHYSICAL PROPERTIES

The different measurement techniques presently used for latent heat of fusion and melting temperature of PCMs may be classified as (i) Drop Calorimeter (DC) (ii) Differential Thermal Analysis (DTA) and (iii) Differential Scanning Calorimeter (DSC). The DC method requires a long time, and the accuracy of the results is not good (Lane, 1989). In DSC & DTA techniques sample and reference materials are heated at a constant rate. The temperature difference between them is proportional to the difference in heat flow between the two materials and the record is called the DSC curve. The recommended reference material is Alumina (Al_2O_3). Latent heat of fusion is calculated using the area under the peak and melting temperature is estimated by the tangent at the point of greatest slope on the face portion of the peak. A number of researchers have used DSC for measuring the thermo-physical properties of the PCMs (Flaherty, 1971; Giavarini et al., 1972; Cantor et al., 1978; Elder et al., 1980; Salyer et al, 1986; Bukovec et al., 1989; Dunn et al., 1989; Aboul-Enein et al., 1991; Takahashi et al., 1991; Babich et al., 1992; Richardson et al, 1993, Gibbs et al., 1995; Feldman et al., 1996; Li et al., 1999; Sharma et al., 1999; Sharma et al. 2002; Liu et al. 2001).

The above methods are, in general, appreciated as an accurate means in measuring the heat of fusion. But the thermo-physical properties of a very small amount (1-10 mg) of the sample PCM might be different from those of the bulk materials including heterogeneous additives. As another method for determining thermo-physical properties of PCM, Zhang et al. proposed a T-history method (Zhang et al., 1999) to overcome the above limitation of DSC. Because this method does not take a small amount of sample, it is very convenient when a cycle test is carried out with sealed tubes containing newly developed PCMs. Nevertheless, the original T-history method has a restriction on accuracy of thermo-physical properties owing to the introduction of some invalid physical assumptions. Hong et al. (2004) tried to improve the accuracy of the T-history method for measuring heat of fusion of various materials. Marin et al. (2003) also improved the Zhang's method to determine temperature-dependent properties. They reported that using this method it is possible to obtain both properties and curves in a simple way which will be of great help in selecting heat storage material and in the subsequent design of a thermal energy storage system. The enthalpy–temperature curves represent an advance for obtaining average properties of the materials as they enable an evaluation of the variation of the thermal properties against temperature.

THERMAL CYCLES

For latent heat storage, commercial-grade PCMs with a purity of about 95% are preferred due to their large-scale availability and low cost. In general, the thermo-physical properties and behavior of commercial-grade materials are found to be very different from those quoted in the literature for laboratory-grade materials (purity more than 99%). Because limited data are available on the effect of thermal cycling on commercial grade PCMs, it is important to study the effects of thermal cycling on the melting temperature, latent heat of fusion and the specific heat of commercial grade PCMs. Sharma et al. (1998; 2002) conducted accelerated thermal cycle tests for latent heat storage materials (stearic acid, acetamide and paraffin wax). They concluded that commercial grade PCMs have shown no regular degradation in their melting points during repeated 1500 thermal cycles. Acetamide and paraffin wax have shown reasonably good stability for the cycling process and can be considered as promising PCMs. Stearic acid melts over a range of temperature. It is recommended that before employing a commercial material as PCM, its thermal cycle test should be conducted as the behavior may change. Ting et al. (1987) conducted accelerated cycle tests on a PCM unit having (Na_2SO_4 .nH_2O) at different ratios by weight. They studied the effect of 1000 thermal cycles on the container tube, but did not analyze its effect on the thermophysical properties of the PCM. Fernanda (1988) has also studied the thermal reliability of salt hydrate PCMs with melting temperatures between 15 and 32 °C by measuring latent heat of fusion and melting temperature after subjection to repeat cycles.

Sharma et al. (2001) tested the effect of thermal cycling on urea and noticed that it did not melt after several cycles. They suggested that urea should not be used as a PCM. Hadjieva et al. (1992) calculated the enthalpy of three paraffin mixtures and found the dependence on their oil content and the distribution of atoms defined by chemical and gas chromatographic analyses. Thermal cycle testing was also carried out for the mixture of technical-grade paraffins and was found to be stable after repeating 900 heating/cooling cycles. Gibbs et al. (1995) reported that paraffin shows excellent thermal stability. Kimura and Kai (1984) used NaCl to improve the stability of $CaCl_2.6H_2O$, containing slightly more water than the stoichiometric composition. The salt was found to be very stable after repeating more than 1000 heating/cooling cycles. Porisino (1988) studied the thermal reliability of salt hydrate PCMs by measuring the latent heat of fusion and melting temperature after subjection to repeated cycles. Wada et al. (1984) investigated the decreasing heat storage capacity of $CH_3COONa.3H_2O$ during thermal cycling and performed calorimetric measurements on three kinds of samples. Hasan and Sayigh (1994) investigated the thermal properties of some saturated fatty acids using the DSC technique after a middle-term period that included heating–cooling cycles 450 times. The thermal energy storage capacity of $Na_2SO_4.10H_2O$ was investigated with respect to thermal cycling by Marks (1980). Zhang et al. (2001) studied the solid-liquid phase transitions in lauric, palmitic and stearic acids and their binary systems. They also investigated the stability of the thermal properties after many heating-cooling cycles, such as 30, 50, 80, and 100. Sari (2003a; 2003b) conducted 1200 accelerated thermal cycle tests to study the thermal reliability of lauric, myristic, palmitic, and stearic acid. Thermal cycling tests have also been conducted for 24 wt% PCM impregnated wallboards. The samples showed no tendency of the PCM (paraffin) to migrate within the wallboard, and there was no observable deterioration in the thermal energy storage capacity (Khudhair et al., 2003).

CORROSION OF THE PCMs

The corrosion of some salt hydrates and salt eutectics on different container materials and their thermal stability were tested (Heine, 1981; Porosini,1988; Groll et al., 1990). Recently, Cabeza et al. (2001a & b; 2004) studied the corrosion resistance of five common metals (aluminum, brass, copper, steel and stainless steel) in contact with molten salt hydrates (zinc nitrate hexahydrate, sodium hydrogen phosphate dodecahydrate, calcium chloride hexahydrate, sodium carbonate, potassium hydrogen carbonate, potassium chloride, water, sodium acetate trihydrate, and sodium thiosulphate pentahydrate) in an immersion corrosion test. Recently, Sari and Kaygusuz (2003) investigated the corrosion resistance of some construction materials to the fatty acids (stearic, palmitic, myristic and lauric acid) over a long period. The material containers were stainless steel (SS 304 L), carbon steel (steel C20), aluminum (Al) and copper (Cu). It was concluded that stainless steel (SS304L) with a chromium oxide (Cr_2O_3) surface layer and aluminum (Al) metals with aluminum oxide (Al_2O_3) surface layers are essentially compatible with the investigated fatty acids based on gravimetric and metallographic corrosion test results. Carbon steel (Steel C20) and copper (Cu) metals, as storage container materials, are preferentially compatible.

HEAT TRANSFER ENHANCEMENT

In a latent heat storage system, the solid-liquid interface moves away from the heat transfer surface during phase change. During this process, the surface heat flux decreases due to the increasing thermal resistance of the growing layer thickness of the molten / solidified medium. In the case of solidification, conduction is the only transport mechanism, and in most cases, it is very poor. In the case of melting, natural convection can occur in the molten layer and this generally increases the heat transfer rate compared to the solidification process (if the layer is thick enough to allow natural convection to occur). However, the generally low heat transfer rate can be increased considerably by using a suitable heat transfer enhancement technique. There are several methods to enhance the heat transfer in latent heat storage system. The use of finned tubes with different configurations has been proposed by various researchers as an efficient means to improve the charge/discharge capacity of a latent heat storage system (Sparrow et al., 1981; Eftekhar et al., 1984; Kamimoto et al., 1986b; Padmanabhan and Murty, 1986; Morcos, 1990; Choi and Kim, 1992; Hoogendoorn and Bart, 1992; Lacroix, 1993b; Khan et al., 1994; Tong et al., 1996; Velraj et al., 1997; Costa et al., 1998; Bauer and Wirtz, 2000). Other heat transfer enhancement techniques are having the PCM inserted in a metal matrix (Stovall et al., 1988; Hafner and Schwarzaer, 1999), using PCM dispersed with high conducting particles (Siegel, 1977), micro encapsulation of PCM (Mulligan et al., 1996; Bedecarrats et al., 1996), embedded graphite matrix (Mehling et al., 1999; Py et al., 2001), carbon fiber brushes with a high thermal conductivity (190 W/mK) (Fukai et al., 2002), exfoliated graphite (EG) for improving the thermal conductivity of the form-stable P/HDPE composite PCMs (Sari et al., 2004), copper plates inserted in spherical capsules for n-octadecane PCM (Koizumi, 2004), using metal screens/spheres placed inside the PCM (Ettouney et al., 2004). Erik and Dudukovic (1996) presented a novel energy storage system consisting of n-octadecane retained by capillary forces in a porous silica support. This configuration eliminates the expensive heat exchange surface, provides higher energy density, and gives higher rates of energy storage and release. Leoni and Amon (1997) employed aluminum foam to enhance the heat transfer process in latent heat storage system.

Encapsulation of PCMs

Encapsulation has two containment methods, macro and micro encapsulation. Macroencapsulation comprises the inclusion of PCM in some form of package such as tubes, pouches, spheres, panels or other receptacles. These containers can serve directly as heat exchangers or they can be incorporated in building products. Previous experiments with macroencapsulation failed due to the poor heat transfer rate. The PCM freezes on the heat exchanger surface resulting in a poor heat transfer rate due to the low thermal conductivity of PCMs. Many attempts have been made to overcome these difficulties. A new technique "microencapsulation" of PCMs was studied in the late 1970s after PCMs had long been employed as the thermal storage and control materials (Colvin, 1999). Microencapsulation is the packaging of micronized materials (both liquids and solids) in the form of capsules, which range in size from less than 1 mm to more than 300 mm. The wall material of the capsule can be formulated by using a wide variety of materials including natural and synthetic polymers. There are many advantages of microencapsulated PCMs, such as increasing heat transfer area, reducing PCM reactivity towards the outside environment and controlling the changes in the storage material volume as phase change occurs.

Macroencapsulation of $CaCl_2.6H_2O$ in plastic and metal containers appears promising for heating systems using air as the heat transfer medium (Lane, 1980). After considering a number of heating and cooling schemes employing phase change heat storage, a forced hot air, central storage design using $CaCl_2.6H_2O$ encapsulated in plastic pipes was adapted. Microencapsulation also allows the PCM to be incorporated simply and economically into conventional construction materials (Fraunhofer ISE, 2002). Plastic or metallic encapsulation of the PCM is expensive but safe, as the PCM is not in contact with the concrete. Microencapsulation by impregnating the PCM in the concrete is very effective, but it may affect the mechanical strength of the concrete. Polymerization of PCMs has been also studied for other applications, like insulation materials for use in clothing or bedding articles (Salyer, 1999). Inaba et al. (1997a) and Lee et al. (1998) proposed shape stabilized paraffin (74% paraffin and 26% HDPE) integrated with the building materials without encapsulation. Structural stability is achieved using HDPE, which retains the paraffin when in liquid phase. Experiments and simulations have been conducted to evaluate the characteristics and performance of encapsulated paraffin in crosslink agents in terms of encapsulation ratio and energy storage capacity (Hawlader et al., 2002). It was found that a higher coating to paraffin ratio led to a higher paraffin encapsulation ratio and then lower product hydrophilicity. Thermal cyclic tests showed that the encapsulated paraffin kept its geometrical profile and energy storage capacity even after 1000 cycles of operation.

A new material for low temperature storage was developed (Royon et al, 1997). They contained the water as a PCM within a three dimensional network of polyacrylamide during the polymerization process. The final material remains well shaped, requiring no support or even coating, so it can be used directly. Recently a compound PCM, which consists of paraffin (75%) as a dispersed PCM and a HDPE (25%) as a supporting material was developed (Hong et al, 2000). The developed PCM (melting point 57 °C, latent heat of fusion 157 kJ/kg) is suitable for application in direct contact heat exchangers. PCM microencapsulation has been developed by many companies (Jahns, 1999). Microencapsulated PCMs can be included within textile fibers; composites and clothing to provide greatly enhanced thermal protection in both hot and cold environments (Colvin et al., 1998). The potential use of microencapsulated PCMs in various thermal control applications is limited because of the cost. However, thermal control for space applications is more important than the cost; researchers believe that the development of such PCMs could be a milestone for space technology (Mulligan et al., 1996).

NEW PCM INNOVATIONS

Revankar (2001) presented a new testing method for satellite power using latent heat storage. PCM becomes liquid under high temperature, which then freezes during hours of cold darkness and releases its latent heat. The released heat can be used to generate electricity by driving thermoelectric units. John et al. (2000) designed a novel ventilation nighttime cooling system (a novel combination of PCM and heat pipes) as an alternative to air conditioning. The system offers substantial benefits in terms of reducing or eliminating the need for air conditioning.

Cabeza et al. (2002) reported that the PCM can be used for transporting temperature-sensitive medications and food because of the PCM's capability to store heat and cold in a range of several degrees. Several companies are engaged in the research of temperature sensitive transporting PCMs for various applications [237 - 241].

Vasiliev et al. (2000) developed the latent heat storage module for motor vehicles so the heat is stored when the engine is stopped, and can be used to preheat the engine on a new start. It is possible to reach an optimized working temperature within the engine in a much shorter time using heat storage than without heat storage. Pal and Joshi (1996; 1997) recommended the PCM to restrict the maximum temperature of electronic components. Tan et al. (2004) conducted an experimental study on the cooling of mobile electronic devices, such as personal digital assistants (PDAs) and wearable computers, using a heat storage unit (HSU) filled with the phase change material (PCM) of n-eicosane inside the device. The high latent heat of n-eicosane in the HSU absorbs the heat dissipation from the chips and can maintain the chip temperature below the allowable service temperature of 50 °C for 2 h of transient operations of the PDA.

Ulfvengren (2004) from Climator has developed a cooling vest for athletes for reducing body temperature. PCMs have also been proposed for cooling a newborn baby (Olsson, 2004). Phase change technologies can also be used for cryosurgery, which is a technique for destroying the unwanted cells by freezing and thawing (Alexiades and Solomon, 1992). Koschenz et al. (2004) developed a thermally activated ceiling panel for incorporation in lightweight and retrofitted buildings. It was demonstrated, by means of simulation calculations and laboratory tests, that a 5 cm layer of microencapsulated PCM (25% by weight) and gypsum surface will maintain a comfortable room temperature in standard office buildings. Paraffins, namely, Hexadecane was tried as a PCM in this prototype set-up. Naim et al. (2002) constructed a novel continuous single-stage solar still with PCM. They reported that the productivity of a solar still can be greatly enhanced by the use of a PCM integrated to the still.

Huang et al. (2004) used PCMs for thermal regulation of building-integrated photovoltaics. Depending on ambient conditions, a PV/PCM system may enable the PV to operate near its characterizing temperature (25 °C). They developed PV/PCM simulation model and validated it with experimental results. The improvement in the thermal performance achieved by using metal fins in the PCM container is significant. The fins enable a more uniform temperature distribution within the PV/PCM system to be maintained. An extensive experimental test has been undertaken on the thermal behaviour of a phase change material, when used to moderate the temperature rise of PV in a PV/PCM system (Huang et al., 2000; 2001; 2002; Tavaranan et al., 2002). Use of PCM with photovoltaic (PV) panels and thermoelectric modules (TEMs) in the design of a portable vaccine refrigerator for remote villages with no grid electricity was proposed by Tavaranan et al. (2002). TEMs, which transfer heat from electrical energy via the Peltier effect, represent good alternatives for environmentally friendly cooling applications, especially for relatively low cooling loads and when size is a key factor. Thermoelectric refrigeration systems employing latent heat storage have been investigated experimentally by Omer et al. (2001). Trelles and Duffy (2003) proposed a numerical simulation of a porous latent heat thermal energy storage device for thermoelectric cooling under different porosities of the aluminum matrix. They used a porous aluminum matrix as a way of improving the performance of the system, enhancing heat conduction without reducing significantly the stored energy.

Weinlader et al. (2004) used PCM in double-glazing façade panel for day lighting and room heating. A facade panel with PCM shows about 30% less heat losses in south-oriented facades. Solar heat gains are also reduced by about 50%. Facade panels with PCM improve thermal comfort considerably in winter, especially during evenings. In summer, such systems show low heat gains, which reduces peak cooling loads during the day. Additional heat gains in the evening can be drawn off by nighttime ventilation. If a PCM with a low melting temperature of up to 30 °C is used, thermal comfort in summer will also improve during the day, compared to double glazing without or with inner sun protection. A homogeneous appearance of the PCM-systems is achievable by use of concealment, like a screen print glazing.

Ying et al. (2004) developed the test standards for PCM fabrics. Three indices have been proposed to characterize the thermal functional performance of PCM fabrics. The index of thermal regulating capability can describe the thermal regulating performance of PCM fabrics, and is strongly dependent on amount of PCM. Khateeb et al. (2004) designed a lithium-ion battery employing a novel phase change material (PCM) for thermal management systems in an electric scooter. Developed Li-ion battery was suggested in order to replace the existing lead–acid battery in the electric scooter without introducing any mechanical changes in the battery compartment.

CONCLUSION

This review will help to find the suitable PCM for various purposes, different techniques for the measurement of thermo physical properties of PCM, suitable heat exchanger with ways to enhance the heat transfer and provide the various designs to store the heat using PCM for different applications i.e. space heating / cooling, solar cooking, greenhouse heating, water heating and waste heat recovery systems. Study on thermal cycles and corrosion of the materials for long term stability is discussed. Recent innovations on PCM applications are included for the awareness about new applications.

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NOMENCLATURE

a_m	Fraction melted
a_r	Fraction reacted
Δh_m	Heat of fusion (kJ/kg)
Δh_r	Endothermic heat of reaction (kJ/kg)
m	Mass of heat storage medium (kg)
T_a	Ambient air temperature (°C)
T_f	Final temperature (°C)
T_i	Initial temperature (°C)
T_m	Melting temperature (°C)
C_p	Specific heat (kJ/kg K)
C_{ap}	Average specific heat between $\mathrm{T_i}$ and $\mathrm{T_f}$ (kJ/kg K)
C_{lp}	Average specific heat between $\mathrm{T_m}$ and $\mathrm{T_f}$ (kJ/kg K)
C_{sp}	Average specific heat between $\mathrm{T_i}$ and $\mathrm{T_m}$ (kJ/kg K)
Q	Quantity of heat stored (kJ)

ABBREVIATIONS

c	Congruent melting
CASE	Compressed air energy storage
EG	Exfoliated graphite
ETSC	Evacuated tube solar collector
HDPE	High density polyethylene
HTF	Heat transfer fluid
ic	Incongruent melting
LHS	Latent heat storage
L	Liquid state
n.a.	Not available
NPG	Neopentyle glycol
PCM	Phase change material
PE	Penaerythritol
PHPS	Pumped hydro power storage
PV	Photovoltaic
SHS	Sensible heat storage
S	Solid state
TAM	Trihydroxy methyl aminomenthane
TEM	Thermoelectric module