REVIEW OF PCMs AND HEAT TRANSFER ENHANCEMENT METHODS APPLIED IN PARABOLIC TROUGH SOLAR PLANTS THERMAL STORAGE SYSTEMS

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ABSTRACT

Solar thermal power generation requires a cost effective thermal storage system. The existing two tank system is very expensive due to the storage material inventory. The use of phase change materials (PCMs) offers higher storage density. A review of potential PCMs was conducted in order to come up with commercially available ones having suitable properties. Most available PCMs have low thermal conductivity making heat transfer enhancement necessary for power applications. The various methods of heat transfer enhancement in latent heat storage systems were also reviewed systematically. The review showed that three commercially-available PCMs are suitable in the operating temperature range of parabolic trough plants. Many heat transfer enhancement methods have been investigated in the literature but the use of aluminium fins is the most promising in the temperature range of 250-330ºC. Many eutectic mixtures of materials have potential for use but discrepancies exist in their reported melting temperature and latent heat of fusion.

Keywords: *Latent heat, high temperature, thermal conductivity enhancement*

1. INTRODUCTION

Solar thermal power generation is one the most sustainable and renewable source of electricity. It has the potential of fulfilling the world's electricity needs due to the availability of solar energy in sufficient quantity in various regions of the world [1 – 3]. Various solar thermal technologies have been developed over the years for the generation of electricity [4]. The parabolic dish [5 – 7] power tower [8, 9] and the parabolic trough [10 – 12] are the most advanced and have been commercialized. The parabolic trough technology using synthetic oil as the heat transfer fluid (HTF) with operating temperature range between 290 and 400ºC is the most matured and cost effective technology for capacities <200 MW. This can partly be attributed to the experience gained in the operation and maintenance of the 354 MW Solar Electric Generating Station (SEGS) plants for over two (2) decades [4, 13]. Most commercial solar plants in operation and under construction are of the parabolic trough technology [9].

The stable and sustainable operation of a solar thermal plant requires a back-up thermal energy source in order to produce thermal energy when that from the sun is insufficient. For cost effective operation there is also the need to avoid energy wastage when the available solar energy is more than required by the power block. This thus makes thermal energy storage system a must for solar thermal plants. The sensible two-tank thermal storage system is the current state of the art with all storage-integrated commercial parabolic trough plants utilizing this technology [9]. This technology is very expensive due to the amount of storage material inventory, requirement of two tanks and the requirement of a costly salt/HTF heat exchanger.

The use of phase change materials (PCMs) offer higher storage density due to the higher latent heat of fusion of the PCMs and higher efficiency since phase change occurs at a constant temperature. Thus PCMs have the potential of smaller and more efficient storage system which can translate into a more cost effective system. The wide operating temperature range of parabolic trough plant using synthetic oil as the HTF requires the use of many PCMs in series in order to fully obtain the benefit of latent heat storage [12 – 14]. This means it is very important to find suitable commercially available PCMs having melting temperature in the operating temperature range of 300 and 400ºC. Research over the years on using PCMs in thermal storage system have shown that there is need for enhancing the thermal conductivity of potential PCMs in order to be able to

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produce latent heat storage systems with high power density and utilization factors [16, 17].

In this study, a review of potential PCMs which were investigated by various researchers over the years was conducted in order to come up with commercially available ones having suitable properties for use in the temperature range of 300 and 400°C. The various methods of heat transfer enhancement that have been investigated over the years were also reviewed.

2. PCM SCREENING

The first most important criteria to consider in selecting a suitable PCM is that its melting temperature must be in the operating temperature range (between 300 and 400°C). Other properties required for a suitable PCM apart from melting temperature are presented in Table 1 alongside the function of each [18]. In selecting a PCM three of these properties must be considered critically because they determine the usability of the material even if it has other favourable properties. These are: reversible phase change, negligible sub-cooling and super-cooling and compatibility with other materials of the system. In general, candidate commercially-available PCMs are either made up of a single material; eutectic mixture of two or more materials or metals and alloys.

2.1 Single Component Phase Change Materials

Potential single component PCMs having melting temperatures in the operating temperature range are limited to low melting point metals such as tin and lead, metallic alloys and inorganic salts [18 – 20]. Low melting point metals and alloys are relatively very expensive even though they have high thermal conductivity [21]. Table 2 presents potential materials

suitable in the operating temperature range from the literature. Only few single materials are available in this temperature range. Rubium Nitrate ($RbNO_3$), Cesium Hydroxide (CsOH) and Lead Bromide ($PbBr_2$) have low latent heat of fusion and thus are not suitable. Magnesium Hydride (MgH_2) is not safe since it reacts violently with air and Indium Bromide (InBr) does not have a completely reversible phase change process [22]. Chlorides have high hygroscopicity, high vapour pressure and corrode steel which is the material used in most components of the storage system [23, 24]. Strong bases such as (Sodium hydroxide and potassium hydroxides) attacks aluminium and cannot be used with heat exchanger having aluminium fins [25, 26]. This thus leaves nitrates of sodium and potassium which are alkali nitrates.

2.1.1 Alkali Nitrates

Alkali nitrate salts have very favourable characteristics in comparison with other materials due to their low rates of corrosion (< 0.01 mm/year), their stability, low vapour pressures, availability and they are relatively cheap making them the most promising [27]. Sodium nitrate is the most extensively studied PCM for high temperature Latent heat Storage (LHS) systems. One of the reasons is that its melting point coincides with saturated steam temperature of water at 100 bar. This condition is suitable for Direct Steam Generation) DSG in parabolic-trough plants.

The melting and latent heat of fusion of $NaNO_3$ reported in the literature ranges from 306 - 310°C and 172 - 200 kJ/kg respectively [31, 32]. Discrepancies can be attributed to the fact that impurities cause reduction in the melting temperature and broaden the melting range [33].

Table 1: Properties of suitable PCM

Physical requirements	
High latent heat of fusion	Smaller storage size for a given capacity compared to sensible heat storage.
High thermal conductivity	To increases the dynamics in the system (rate of heat transfer).
Reversible Phase change	For cyclic operation.
Negligible sub-cooling and super-cooling	This is to make sure that the freezing and melting takes place at the same temperature.
High Density	Smaller storage size
Technical Requirements	
Small density change	To reduce the amount of unfilled space in the PCM container.
Low vapour pressure	To eliminate the need for pressurized container.
Chemical stability and compatibility with other materials of the system	To ensure the long term use of the system.
Economic requirements	
Low specific cost and availability	To ensure it will be cost effective.
Non-toxic and recyclable	To ensure they are environmentally friendly

Table 2: Potential single component PCMs for parabolic trough plant using synthetic oil as HTF

Material	Melting Temperature (average), °C	Latent Heat of Fusion (kJ/kg)	Density (at room temperature) kg/m³	Thermal Conductivity (W/mK)	
				Solid	Liquid
$NaNO_2$	270	180	1810	0.67-1.25	0.53-0.67
$ZnCl_2$	280	75	2907	0.5	
InBr	297	133			
$RbNO_3$	305	38	2519		
$NaNO_3$	307	176	1900	0.59	0.51-0.57
NaOH	323	165	2130	0.92	
TlF	326	62	8300		
MgH_2	327	532	1450		
KNO_3	337	100	1865		0.42-0.50
CsOH	342	52	1720		
KOH	360	134	2040		
$PbBr_2$	371	45	5730		

Source [16, 28 - 30]

Bauer, *et al*. [34] has conducted an experimental study on the suitability of sodium nitrate as a high temperature PCM. $NaNO_3$ was reported to have a melting temperature of 306°C and an average heat of fusion of 177 kJ/kg. $NaNO_3$ is stable up to 450°C, above which it start to form sodium nitrite and oxygen. It has an average percentage change in volume during melting of 9.7%. Thermal stability at 350°C for long time has been tested in German Aerospace Centre (DLR) with small production of nitrite. It attacks graphite and as such cannot be used with graphite fins [34]. $NaNO_3$ has been tested in an 8.51 kWh theoretical capacity experimental LHS system having aluminium fins for about 172 cycle's equivalent to about 4000 hours of operation without any problem [35].

Potassium nitrate (KNO_3) has a reported melting temperature range of 333 –337°C and latent heat of fusion ranging from 91 – 98.9 kJ/kg in the literature [18, 28, 36, 37]. Geyer [38] reported a latent heat of fusion of 266 kJ/kg. This value is different from all the values reported in the literature. Experiments conducted using DSC gave a latent heat of fusion of 97.25 kJ/kg and a melting temperature of 335.32°C [24]. This is close to what has been reported in most literatures. KNO_3 being an alkali nitrate will have corrosion, compatibility and thermal stability properties similar to $NaNO_3$. It has a volume expansion of 3.3% which is very good since small volume change is good for LHS system. Overall $NaNO_3$ and KNO_3 are suitable for use as PCMs since they are thermally stable, compatible with other materials of the system and are not expensive.

2.2 Multi-Component Phase Change Materials

From Section 2.1, it can be concluded that there are very few suitable single component PCMs for use in LHS system and thus eutectic mixtures of two or more salts to produce a suitable PCM are required. Multi-component mixtures of salts tend to have higher latent heat of fusion than single component PCMs [21]. They have the potential of smaller and cheaper system than the single component PCMs. The main challenge of eutectic salt mixtures is finding the eutectic composition and thermal properties of the mixture especially the melting temperature and latent heat of fusion [20]. Tables 3 and 4 present composition and available thermo-physical properties of eutectic mixtures of salts suitable for the operating temperature range. Properties presented in Table 3 were obtained using either the FactSage 6.2 thermochemistry [39] software or the phase change diagram of the mixture by Gomez [30]. The materials presented in Table 4 were obtained from literature data since 1960 compiled by Kenisarin [37]. These properties must be confirmed by experiments since some composition and properties reported in the literature do not agree with that obtained using thermo-chemistry software or phase change diagrams.

Experiments conducted by Gomez [20] using a Differential Scanning Calorimeter (DSC) confirms the presence of discrepancies in the reported composition, melting point and latent heat. One of such discrepancy is the non-existence of the melting temperature of 342°C for the eutectic mixture of KNO_3 (80.69), KBr (11.87) and KCl (7.44) % by mass and latent heat of fusion of 140 kJ/kg. Experiments confirm that the mixture melt over a range of temperature which is in conformity with the result from FactSage 6.0 software and phase diagram.

In this section the multicomponent PCMs that have been investigated or used successfully for LHS systems will be discussed in order to come up with the most suitable commercially-available PCMs that can be used in the LHS system.

Table 3: Potential eutectic salt mixtures for parabolic trough plants using synthetic oil as HTF obtained using FactSage software and phase equilibrium diagram

Composition of salt mixture (by mass %)			T_m (°C)	ΔH (kJ/kg)	Cp (J/gK)	
					Solid	Liquid
Binary Mixtures						
KNO_3 (92.82)	KCl (7.18)		307.87	105.63	1.156	1.177
KNO_3 (65.31)	K_2CO_3(34.69)		325.73	71.58	0.812	0.823
LiBr (52.26)	KBr (47.74)		327.8	333.05	0.562	0.672
KNO_3(91.15)	KBr (8.85)		329.84	100.93	1.161	1.161
$FeCl_2$(52.08)	KCl (47.92)		350	133.91	0.706	0.938
KCl (54.75)	LiCl (45.25)		352.53	267.96	1.009	1.279
K_2CO_3 (22.05)	KOH (77.95)		365.5	164.35	1.332	1.394
K_2SO_4 (16.54)	KOH (83.46)		376	174.09	1.329	1.408
$FeCl_2$ (63.02)	NaCl (36.98)		376	249.54	0.768	0.983
Ternary Mixtures						
$MgCl_2$ (42.05)	KCl (39.07)	NaCl (18.88)	331.31	198.45	0.857	1.031
$MgCl_2$ (46.23)	KCl (39.90)	NaC l(22.87)	331.87	207.14	0.859	1.033
NaCl (22.24)	KCl (28.80)	$FeCl_2$ (48.96)	332.55	308.88	1.326	1.695
$CaCl_2$(10.37)	KCl (53.11)	LiCl (36.52)	338.36	241.24	0.950	1.200
$MgCl_2$(42.90)	KCl (48.14)	NaCl (8.96)	380.95	177.27	0.752	0.946
KCl (57.2)	LiCl (36.5)	LiSO4 (6.3)*	324			
KF (54.0)	AlF_3 (6.2)	ZrF_4 (39.8)*	380			
Na_2SO_4 (28.4)	K2SO4 (17.4)	$ZnSO_4$ (54.2)*	385			
*Percentage by Mol.						

Table 4 Potential eutectic salt mixtures of from the literature since the 1960s

Composition of salt mixture (mol%)				T_m (°C)	ΔH (J/g)
Binary Mixtures					
LiCl (59.15)	$Ca(NO_3)_2$ (40.85)			270	167
LiOH (65.5)	LiCl (34.5)			274	339
$NaNO_3$ (93.6)	NaCl (6.4)			284	171
$NaNO_2$(54.8)	KNO_3(45.2)			285	152
KNO_3 (13)	$Ba(NO_3)_2$ (87)			290	124
KNO_3 (33)	$RbNO_3$ (67)			292	
NaF (3.5)	$NaNO_3$ (96.5)			304	
NaCl (6.3)	NaOH (93.7)			314	
LiOH (40)	KOH (60)			314	341
KNO_3 (94)	KCl (6)			320	150
LiCl (58)	KCl (42)			348	170
Ternary Mixtures					
LiOH (62)	LiCl (36.5)	KCl (1.5)		282	300
NaOH (85.8)	NaCl (7.8)	$Na2CO_3$ (6.4)		282	316
Na_2SO_4 (5.3)	NaCl (8.4)	$NaNO_3$(86.3)		287	176
NaCl (8)	NaF(5)	$NaNO_3$ (87)		288	224
LiCl (54.2)	$BaCl_2$ (6.4)	KCl (39.4)		320	170
KNO_3 (80)	KBr (10)	KCl (10)		342	140
NaCl (33)	KCl (24)	LiCl (43)		346	281
KCl (28.7)	$MgCl_2$ (45)	NaCl (26.3)		350	215
Quaternary Mixture					
LiF (7)	LiCl (41.5)	$LiVO_3$ (16.4)	Li_2CrO_4 (35.1)	340	177

Source [36]

2.2.1 KNO₃/KCl

Dinter *et al.* [14] reported an eutectic mixture of KNO_3/KCl (6% by mol, 4.5% by mass) having a melting temperature and latent heat of fusion of 320°C and 150 kJ/kg respectively. From Table 3 an eutectic mixture with 7.18% by mass KCl was reported to have a melting temperature and latent heat of fusion of 307.87°C and 150.63 kJ/kg respectively using FactStage software

[20]. Experiment conducted by Michels [40] using DSC showed that an eutectic mixture with 4.5% (by mass) KCl has a melting temperature and latent heat of fusion of 320°C and 74.4 kJ/kg respectively. Also Glatzmaier, *et al.* [24] obtained a melting temperature of ~320°C and latent heat of fusion of about 82.86 kJ/kg using DSC and showed that it is the best candidate PCM for temperature bucket around 320°C after considering various eutectic mixtures.

This confirms the correct properties and clears the discrepancy. Since this eutectic mixture has 96.5% by mass KNO_3, it will thus be expected to have similar characteristics with KNO_3 thus proving its suitability for LHS systems. The difference in the latent heat of fusion of 74.4 kJ/kg and 82.86 kJ/kg may be due to impurities and experimental errors.

2.2.2 Mixture of KNO₃, KBr and KCl

SERI [19] has presented an eutectic composition of 80.69% KNO_3, 11.87% KBr and 7.44% KCl (percentages by mass) having a melting temperature of 342°C and latent heat of fusion of 140 J/g. From the FactSage software and phase diagrams for ceramist, Gomez [20] reported that this mixture does not have a particular melting temperature but melts over a range of temperatures. Experiments conducted proved this and the mixture has a melting temperature ranging from 326.58°C to 412.99°C with a latent heat of fusion (average) of 75.89 J/g which is not same as that reported by SERI [19]. Thus this mixture cannot be used as a PCM.

2.2.3 Mixture of NaCl, KCl and LiCl

From the literature this has an eutectic mixture with a composition of 34.81% NaCl, 32.29% KCl and 32.90% LiCl (% by mass) having a melting temperature of 346°C and latent heat of fusion of 281 J/g [19]. Experimental investigation on corrosion at 500°C showed that this mixture corrodes stainless steel (SS316L) and attacks aluminium [20]. Experimental investigations [20] showed that the mixture has an average melting point of 351.36°C with average super-cooling of 1.20°C. This is about 5°C higher than that reported by SERI [19] and may be due to the purity or method employed in making of the mixture. A value of latent heat of fusion (average) of 131.96 J/g with a standard deviation of 9.32 was obtained and a latent heat of solidification of 123.71 J/g with a standard deviation of 0.86 was obtained. Even though the standard deviation for the latent heat during melting is very high and brings doubt to the accuracy of the result the value is much less than that reported in SERI [19]. This result has to be collaborated with other experimental result in order to confirm the exact latent heat.

2.2.4 Mixture of MgCl₂, KCl and NaCl

From literature this has an eutectic composition of 60% Magnesium Chloride ($MgCl_2$), 20.4% Potassium Chloride (KCl) and 19.6% Sodium Chloride (NaCl) (% by mass) with melting temperature of 380°C and latent heat of fusion of 400 J/g [14]. This mixture was found to highly corrode stainless steel (SS316L) and attack aluminium metal. Investigation of the of the properties of the mixture resulted in an average melting temperature of 381.47°C with a standard deviation of 0.79 and an average latent heat of fusion of 198.55 J/g. This shows that the value for the melting point presented in the literature was correct but the latent heat of fusion reported was too high which is about double the actual value [20].

3 HEAT TRANSFER ENHANCEMENT METHODS

During discharging, in a LHS system, a solid layer of the PCM forms around the HTF pipes which insulates the pipe leading to decrease in heat transfer. Michels and Pitz-Paal [16] demonstrated that increasing the thermal conductivity of the PCM in both phases from 0.5 to 2 W/mK reduced the amount of PCM required in a five stage cascaded storage system ($NANO_3$, KNO_3/KCl, KNO_3, KOH and $MgCl_2$/KCl/NaCl) by ~40% and makes the amount of storage material required for an 875 MWh_{th} capacity storage system to be 15% less than that of a molten-salt two-tank system in the Andasol 1 plant. The amount of the storage material forms part of the major cost of the two-tank system. The increase in thermal conductivity will also reduce the number steel HTF-pipes required. Steinmann et al. [23] demonstrated that ~50% reduction in the number of pipes required is obtainable, if the thermal conductivity in both phases of the PCM is increased from 1 W/mK to 10 W/mK.

Various methods can be used to increase the thermal conductivity of PCMs. These can be broadly classified into three:
• Use of composite materials (micro encapsulation)
• Use of extended surfaces
• Use of thermo-syphon/heat pipes

These methods have been studied extensively for low temperature applications [41; 42]. In the following sections, these methods of heat transfer enhancement for high temperature applications were discussed.

3.1 Composite Materials (Micro Encapsulation)

This entails mixing the PCM with a material having very high thermal conductivity to form a composite material

with higher thermal conductivity than the original PCM. In a typical storage module the composite is produced as a solid with holes through which the HTF pipes will pass (Figure 1). This method does not require an encapsulation container.

Figure 1: Micro encapsulated PCM [25]

Table 5: Thermal conductivities of PCM/Graphite composites produced by Morrisson et al. [49]

Composite composition (% CEG)	Thermal conductivity (W/mK)	
	Axial direction	Radial direction
0	0.8	0.8
3.96	1.6	4.1
5.27	2.6	5.65
7.35	2.8	8.2

Source [49]

Various methods can be used for the production of PCM composites:

- Infiltration or impregnation in which the PCM is absorbed into the pores of a porous high conductivity material such as expanded graphite to form a composite [44, 44].
- Dispersion which involves mechanically mixing the solid PCM with powder of a high conductivity material and then melting it to form a composite or dispersing the high conductivity material powder in melted PCM [45 – 47].
- Electro-spinning involves the production of nano/micro fibres of a PCM metal composite by using electromagnetic field [48].
- Cold compression involves compressing a mixture of the solid PCM with the high thermal conductivity material powder at ambient temperature to form a solid composite. This method do not require thermal energy during production and there is no corrosion of equipment [45].

The infiltration method is the most widely used technique and the most suitable high conductivity material for use is expanded graphite since it is chemically stable, have high thermal conductivity and high porosity [18].

The production of PCM composites for high temperature applications have been conducted by various researchers. Morisson *et al.* [49] produced PCM/CNEG composites using an eutectic mixture of KNO_3/$NaNO_3$ as PCM by using the infiltration method without any significant loss in latent heat of the PCM. Table 5 presents the axial and radial thermal conductivities obtained for different percentage mass of Compressed Naturally Expanded Graphite (CNEG) in the composite. The use of 3.96% by mass of expanded graphite resulted in 74% reduction in the number of steel HTF-pipes required, compared with a similar storage using the pure PCM.

Pincemin *et al.* [45] used the infiltration method for the production of a $NaNO_3$/KNO_3-ENG (Expanded Natural Graphite) composite by soaking of the graphite matrix in the melted PCM under atmospheric and vacuum conditions, at industrial and lab scale. After 15 hours of soaking, ~40% by volume of the graphite pores is empty. This thus shows the inefficiency of the infiltration method. Similarly, Steinmann, *et al.* [50] asserted that it is impossible to infiltrate graphite with inorganic-salt PCM.

The cold compression method has also been used in the development of composite material using KNO_3/$NaNO_3$ as PCM and expanded graphite by Pincemin, *et al.* [45] and Steinmann, *et al.* [49]. Pincemin et al. [43] result showed that a composite with 20% ENG has a radial thermal conductivity of 40 W/mK and 22 W/mK at 47°C and 200°C respectively. This is about 31 times increase in the thermal conductivity at 200°C compared to that of the pure PCM. Reduction in the specific latent heat was also observed. Steinmann, *et al.* [50] tests showed that separation between the graphite and the salt (PCM) occurs during cyclic operation. This may be due to salt expansion; moisture and impurities in the PCM; and good wettability of the PCM with metals meaning high propensity for the occurrence of creeping.

The dispersion method has also been tried by putting graphite flakes of different sizes in molten KNO_3/$NaNO_3$ [51]. Axial thermal conductivities ranging from 3.5 to 9 W/mK were obtained for 20% by weight of graphite corresponding to a 14 times increase at room temperature. The difference in thermal conductivity was due to the size of the flakes. Reduction in the latent heat of between 5% and 28% depending on the flake size was also observed. The

thermal conductivity were found to reduce with increasing temperature by 2.25 %/°C. Thus at 220°C which is the melting point of the PCM, the thermal conductivity was 6 W/mK for 20% by weight graphite. In summary, the infiltration, cold compression and dispersion methods have all been tested and results clearly showed that the use of graphite to form PCM composites improves the thermal conductivity of the resulting composite. The higher the graphite content, the higher the thermal conductivity of the composite. There is a reduction in the thermal conductivity with increase in temperature leading to requirement of higher amount of graphite (more than 10%). For cost effective composite material, the mass fraction of graphite is limited to 5% [50, 52]. Reduction in the specific latent heat was observed and separation of the PCM from the graphite occurred during cyclic operation. Thus the use of micro encapsulation with nitrate-salt PCM is not a viable heat transfer enhancement method in high temperature LHS system.
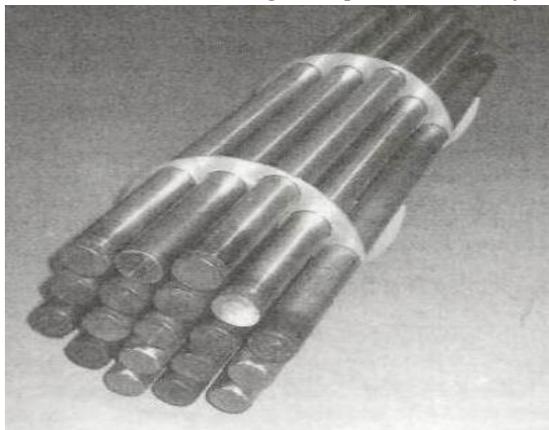

Figure 2: Macro encapsulation of PCM [25]

3.2 Extended Surfaces

3.2.1 Macro encapsulation

Macro encapsulation involves enclosing the PCM in small casings which can either be spherical or cylindrical in shape. Cylindrical containers are easier to manufacture. These small casings are then arranged in a vessel filled with pressurized water/steam or the HTF. Characteristic diameters of these casings range from 5 to 20 mm. To ensure that these capsules can survive the corrosion by the PCM for at least 10 years, a minimum of 1 mm wall thickness casings must be used. Since the PCM expands during melting by about 10%, space must be provided for this expansion by adding gas to the capsule. Cylindrical capsules of 0.5 m length and 7.5-12.5 mm radius range, using a mixture of KNO_3-$NaNO_3$ as the PCM, have been prepared and tested in DLR under the DISTOR (Energy Storage for Direct Steam Solar Power Plants) project (Figure 2). Many charging and discharging cycles were achieved

showing the feasibility of the method. It was found out that a lot of steel material (almost equal to the mass of the PCM) is required, manufacturing the capsules is complex and the proportion of PCM in the system is <40%. This makes it very expensive and not a promising option [50, 52].

3.2.2 Sandwich Concept

The use of fins, which is referred to as the sandwich concept, is the most promising option of all the heat transfer enhancement methods for temperatures >200°C [35, 50]. The common configuration of circumferential fins mounted on the HTF pipes is employed. Various materials with high thermal conductivity have been considered for the fin material, such as stainless and low carbon steel, graphite, copper and aluminium. Graphite and aluminium are regarded as the best options out of these because of their high thermal conductivity and low specific cost [50]. Graphite is chemically stable for temperatures up to 250°C in nitrate and nitrite salts and when in contact with steel pipes galvanic corrosion does not occur [51, 53]. Three experiments have been conducted in the DISTOR I, PROSPER and DISTOR II projects using fins made up expanded graphite foil for thermal storage capacities of 3.5, 7 and 55 kWh$_{th}$, respectively. Table 6 presents the details of the three storage units. Many charging and discharging cycles were achieved without any graphite degradation, thus proving the feasibility of the concept [53]. In the PROSPER a storage temperature of 155°C was used for heating saturated water from 125°C to superheated steam at 145°C (at the beginning of discharging) and saturated steam at 125°C (at the end of discharging).

Thermal power of ~8 kW$_{th}$ was achieved for most part of the process. In the DISTOR II, average power of 90 kW$_{th}$ and 35 kW$_{th}$ were obtained over a period of 1 hour for the charging and discharging respectively [50]. Laboratory test have also been conducted at DLR in 2008 with a 37 MJ capacity module (Figure 3) having seven finned HTF-pipes with a height of 1.4 m and diameter of 0.308 m using sodium nitrate, having melting temperature of 306°C (Table 6). Aluminium fins were used since graphite is not compatible with the nitrate salt. The module was tested for more than 4000 hours corresponding to 168 charging/discharging cycles (3.5 hours charging and 2.5 hours discharging) for temperatures between 290 and 330°C [53]. In a typical cycle, 7.87 kWhth and 7.20 kWhth were stored and discharged respectively.

Table 6 : Test storage modules using graphite fins [53]

Project	Maximum Power (kW)	Capacity (kWh)	PCM	PCM Mass (kg)	Melting temperature (^{o}C)	HTF
DISTOR I	2	3.5	$KNO_3/NaNO_3$	130	225	Thermal oil
PROSPER	15	7	$KNO_3/NaNO_2/NaNO_3$	400	145	Steam from test facility
DISTOR II	100	55	$KNO_3/NaNO_3$	2000	225	Steam from parabolic trough

During discharging an average specific power of 42.5 kW_{th}/m^3 was achieved. Degradation in melting temperature was not observed and the aluminium fins did not show any sign of degradation [35, 53]. Thus Aluminium is chemically stable in nitrites and nitrates for temperatures up to 330°C. A 700 kWh_{th} capacity LHS module using $NaNO_3$ as PCM and aluminium fins has been constructed and tested successfully in a three stage storage system suitable for DSG plants [54, 53].

Figure 3: Test storage module using NaNO₃ PCM showing the full module and the fins [35]

Figure 4: Heat pipe working principle [54]

It can be concluded that the sandwich concept using graphite fins at temperatures below 250°C and aluminium fins in the temperature range of 250-330°C is a feasible way of solving the problem of the low thermal conductivity of PCM.

3.2.3 Heat Pipe/Thermo-Syphon

Heat pipe consist of a tube closed at both ends with a small amount of working fluid inside the tube. The interior of the tube is lined with a wick that transfers liquid due to capillary action. Figure 4 presents a schematic diagram showing the working principle of a vertical heat pipe. The end of the tube where heat is applied is called the evaporator and when heated the working fluid vaporizes and moves to the other end of the tube. At this end of the heat pipe, the heat of vaporization is released through the tube wall causing the working fluid to condense into liquid. The wick then transports the liquid back to the evaporator and the cycle is repeated.

For vertical tubes the liquid can also be transported by gravity (there is no need of a wick). Since latent heat of evaporation is used, high heat transfer rates can be achieved using a small temperature difference (almost isothermal). Heat transfer rates improvements of up to 90 times greater than bare copper tubes have been obtained for copper-water heat pipes in cooling of electronic devices [57].

Heat pipes have been applied in LHS systems for low temperature (<100°C) applications [56 – 59]. By employing a thermal network model, Shabgard *et al.* [60] showed that heat pipe has the potential of enhancing the heat transfer rates in large-scale LHS system for parabolic-trough plants using synthetic oil as HTF. Economic analysis conducted by Robak, *et al.* [61] showed that 15% potential decrease in capital cost is obtainable compared to the commercially available two-tank system. However, there is still the need for the demonstration of the real feasibility of such system and the long term corrosion and stability of the welded heat pipes.
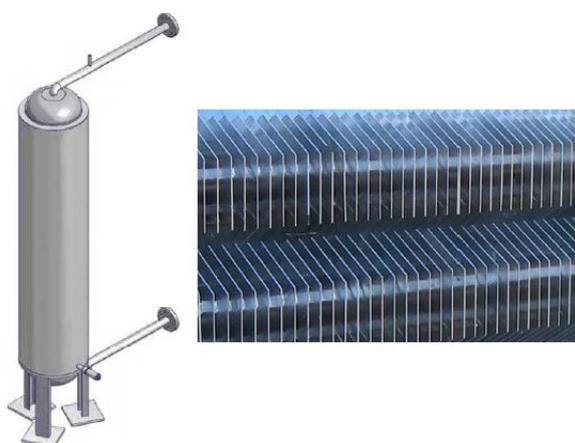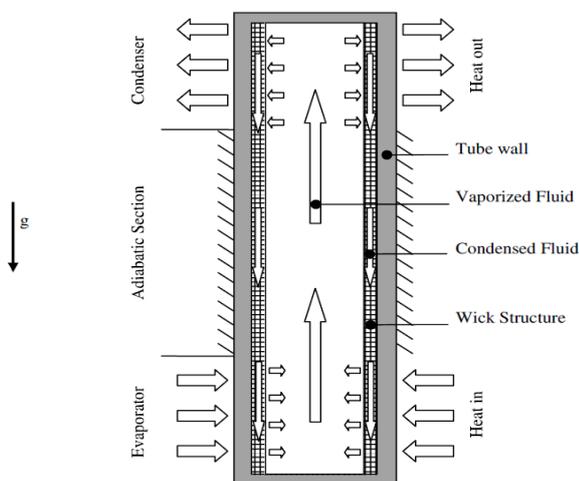
Table 7: Thermo-physical properties of suitable PCMs

	NaNO$_3$		KNO$_3$/KCl (4.5% by mass)		KNO$_3$	
	Solid @ 20 °C	Liquid @ melting	Solid @ 20 °C	Liquid @ melting	Solid @ 20°C	Liquid @ melting
Melting temperature (°C)		306		320		335
Latent heat of fusion (kJ/kg)		171.8		74.4		95.2
Density (kg/m^3)	2261	1910	2100	1850	2109	1870
Specific heat capacity (kJ/kgK)	1.096	1.823	1.21	1.21	953	1342
Thermal conductivity (W/mK)	0.495	0.565	0.48	0.48	0.5	0.459
Dynamic viscosity (kg/ms)		3.02x10^{-3}				2.97x10^{-3}
Thermal expansion coefficient (1/K)		3.65x10^{-4}				4.16x10^{-3}
Volume expansion (%)		10.7		14.1		3.3

Source [40]

Using the principle of thermo syphon, Adinberg *et al.* [62] developed a novel concept called the RHTS concept in which a secondary-HTF just like the working fluid in the thermo syphon is used for the exchange of thermal energy between the PCM and the HTF (water) for the production of superheated-steam in the 350-400°C temperature range. Zinc-tin alloy with a melting temperature of 370°C was used as the PCM. Figure 5 presents the schematic diagram of the RHTS system consisting of two heat exchangers for charging and discharging. The PCM is situated at the middle with embedded vertical channels linking the bottom with the top.
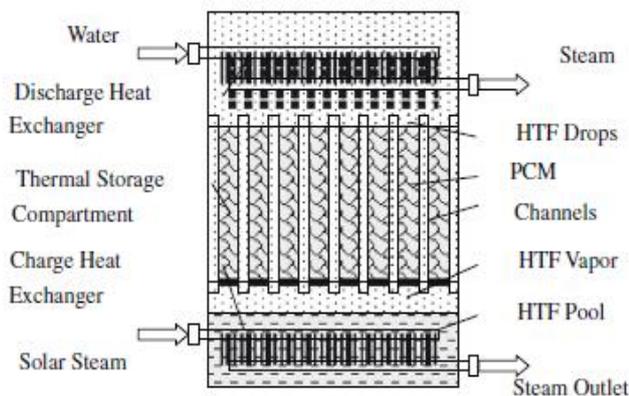

Figure 5 The novel reflux heat transfer storage (RHTS) system concept [60]

During charging, steam is passed through the bottom heat exchanger which is situated in a pool of the secondary HTF, thus boiling the secondary-HTF leading to its evaporation through the channels in the thermal storage compartment. As the secondary-HTF pass through the compartment, the solid PCM is heated and it melts leading to the condensation of the secondary HTF back into the pool. During discharging, water is converted to steam in the top heat exchanger (steam generator) by evaporation of the secondary-HTF by the already heated PCM. The chemical stability and thermal cycling of the HTF and Therminol VP-1 (secondary-HTF) has been tested successfully and simulation of a 12 MWe pilot plant with integrated storage showed the feasibility of the system. The proposed PCM (Zn-Sn alloy) is very expensive compared to inorganic salts.

4 CONCLUSIONS

There are very few materials having melting temperature in the operating temperature range of the parabolic trough plants using synthetic oil as HTF. Alkali nitrates and nitrate are the most suitable PCMs for use in LHS systems. Many eutectic mixtures of materials have potential for use but the main challenge with eutectic mixture is the correctness of the melting temperature and latent heat of fusion reported in the literature. Thus properties of material must be confirmed using experiments before a PCM can be termed suitable. Many of the potential eutectic mixtures are chlorides and hydroxides both of which corrode steel, hydroxides attack aluminium and chlorides have high vapour pressure. This has limited their suitability. In view of this only three commercially-available PCMs are suitable in the operating temperature range whose properties have been confirmed experimentally. Table 7 presents the thermo-physical properties of these materials. There is need in finding other PCMs with high latent heat of fusion preferably mixtures containing more of nitrates since they are the most suitable.

The use of aluminium fins is the most promising method for heat transfer enhancement in the 250-330°C temperature range since it has successfully been tested in various lab and industrial scale experiments.

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