Review on Thermal Energy Storage Using Phase Change at High Temperature: Materials Selections and Applications

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ABSTRACT

There is increasing awareness that there are limits to availability of nonrenewable resources while there is an increasing energy demand throughout the world. However world facing the challenge of variable renewable energy outputs due to sophisticated feature of the energy sources. Thermal energy storage (TES) can be good option to overcome this energy sources. Thermal energy storage in general and phase change materials (PCM) have been a main topic in research for last 30 years. The objective of this paper is to present an overview about history of the thermal energy storage system using phase change materials and its selection criteria, and its various applications at high temperature. The review considered the art in research and developments of high temperature phase change material for high temperature storage in the range of temperature range up to 120 to 1200 ^{0}*CThis studied information will be very helpful to researchers and engineers in energy storage industry.*

Keyword: - *Thermal energy storage (TES), Phase change material (PCM), latent heat storage, phase change etc.*

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1. INTRODUCTION

Fossil fuels play a significant role in the modern society. Used primarily for heat and production for the residential and commercial applications. This fuels eventually emits greenhouse gases which responsible to climate change and global warming. The renewable or low grade waste energy resources can be the solar, wind, biomass and industrials low temperature waste energy. The utilization of the thermal energy storage which has greatly attracted the scientific and industrial community, can be a good option for the energy conservation and management to relieve the energy challenge nowadays. TES can narrow the gap between the global energy demand and supply in various applications. Thermal energy storage can be stored in the sensible and latent heat using phase change materials. Latent heat storage is deeply discussed in this paper. Thermal energy storage (TES) in general and phase change materials have been a main topic in research for last 30 years. The work described in this study deals with energy saving, the efficient and rational use of available resources and optimum use of renewable energies.
Thermal energy storage provides solutions in very specific areas:

The time delay and available power between production or availability of energy and its consumption in receiving systems solar energy, cogeneration etc. and security of energy supply.

This paper provides a review of studies dealing with TES using phase change materials selection, applications and heat transfer enhancement techniques of TES.

A thermal energy storage system mainly consist of three parts, storage medium, heat transfer mechanism and container systems. TES stores energy in the form of sensible, latent or vaporization. Nowadays latent heat storage is mostly used using phase change material. The purpose of the heat transfer mechanism is stands for supply or extract the heat from the storage medium. Container system consist the storage medium as well as the energy heat transfer mechanism. Depending on the type of storage the several requirement must be considered to ensure optimal storage longevity. Which are as follows:

High energy density in the storage materials

Good heat transfer between n the heat transfer mechanism and storage medium

Mechanical and chemical stability of the storage material

Chemical compatibility

Complete reversibility for large number of charging and discharging cycles

Low cost

Low thermal losses

Lower environmental impact

1.1 Phase change materials

Storage systems based on phase change materials with solid–liquid transition are considered to be an efficient alternative to sensible thermal storage systems. From an energy efficiency point of view, PCM storage systems have the advantage that they operate with small temperature differences between charging and discharging (Fig. 1). Furthermore, these storages have high energy densities compared to sensible heat storages.

The most interesting phase change to be applied in a thermal storage is the phase change solid–liquid. Fig. 2 shows a scheme with the families of materials which could be used as phase change materials in thermal energy storage systems. The development of effective thermal energy storage systems using PCM is increasing the interest, due to the potential improvement in energy efficiency, storing and releasing thermal energy at nearly constant temperature [1]. But most PCM have low thermal conductivity, and that leads to slow charging and discharging rates.

The melting temperature is the main parameter to be considered for an appropriate selection of the PCM: it has to lie within the practical range of the selected application. Agyenim et al. [2] presented an overview of the PCM properties and related applications studied in literature.

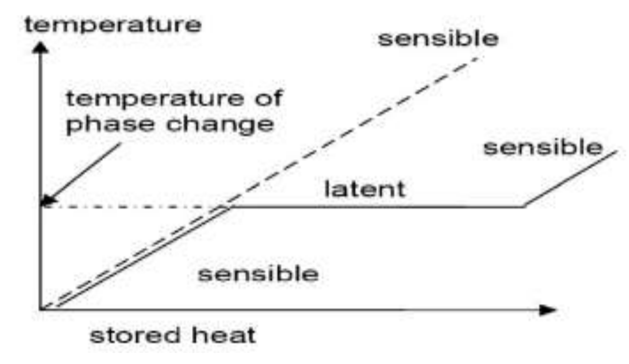

Figure 1 Phase Change phenomenon

1.2 Classification

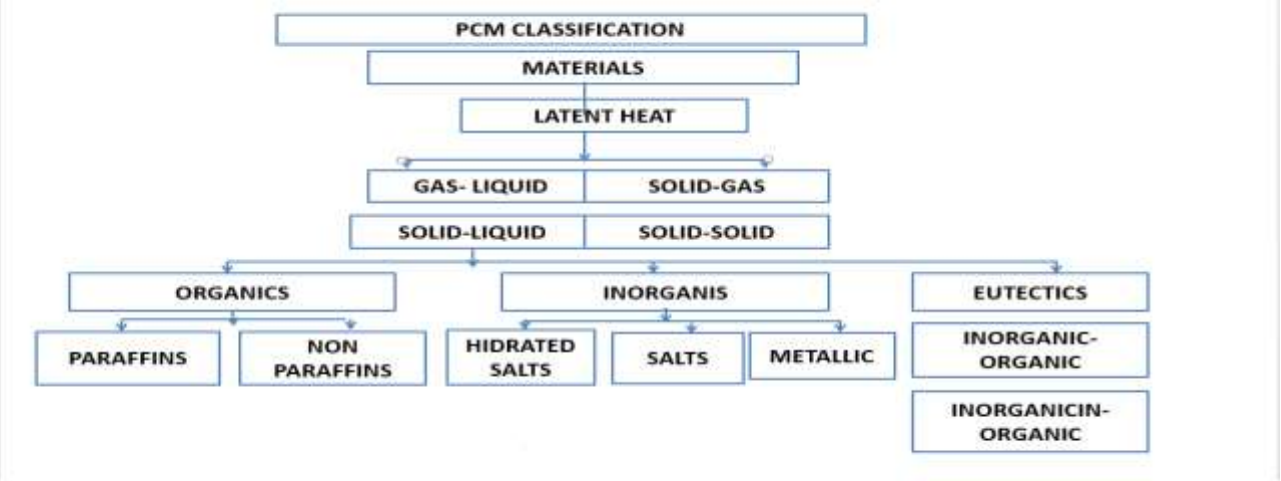

Figure 2 Classification of PCM

The applications were subdivided in three subclass in terms of operating temperature range:

Low temperature: 0–65 C. Suitable PCMs are Paraffin, water/ice, stearic acid, n-octadecane;
Medium temperature: 80–120 C. Appropriate PCMs are Erythritol, RT100, MgCl26H2O;
High temperature: >150 C. Adequate PCMs are $NaNO_3$, KNO_3, NaOH, KOH, $ZnCl_2$.

1.3 Organic/ inorganic materials

A comparison of the advantage and disadvantages of organic and inorganic material disused in table 1. Inorganic materials are hydrated salts, nitrates salts, fluoride and chloride salts. Which are commonly used in the field of solar thermal energy storage in concentrated power plants and also in solar cooking as well as waste heat recovery plants. Lane et al [3] there is extensive review of phase change materials and especially hydrates salts. Murat M et al **[4]** reviewed all hydrates and nitrates, chlorides salts very exhaustive. A significant number of authors have based their work on inorganic salts. Organic materials are mostly used in low temperature which are class called MCPCM (phase change materials which is made of molecular alloys). This review study mainly focused on high temperature phase change materials which are inorganics salts.

2. Selection criteria of material

The demanded melting temperature which provides operating the storage unit in desirable interval of working temperature

High specific thermal conductivity heat of fusion and density to provide the minimum size of heat storage unit

PCM should keep stoichiometric composition in solid and liquid condition. Otherwise distinction in solid and liquid phase appeared at fusion which lead to separation of fusion

Reliable convertibility at repeated phase change conditions

High heat conductivity providing the minimum temperature gradients demanded for charging and discharging of heat storage unit

The minimum change in volume at transition from one phase in another that allow the simple forms of container and heat exchanger.

Insignificant overcooling during hardening

Chemical stability

They must be nontoxic or little toxic

Flame and fire safety

Ease availability and cost effective

2.1 Salts and salt compositions

2.1.1 Choice of salts and salts compositions to be perspective for het storage

From the requirements imposed upon phase change heat storage materials (HSM), it is seen that they, first of all, should has suitable melting temperature and, whenever possible, high heat of fusion. In a considered interval of temperatures, the great interest represent the inorganic salts, the melting temperature of which lays in the range from 250 to 1680 ^{0}C, and heat of fusion from 68 to 1041 J/g. gives the basic group of salts that serve as origin materials in work of high temperatures. Besides fluorides and chlorides, the compositions on the basis hydroxides, nitrates, carbonates and other salts represent the considerable interests

Salt composition (mol.%)	Tm,^{o}C	ΔHf, J/g
Hydroxides		
NaOH(50)-50KOH	169-171	202-213
LiOH(30)-70NaOH	210-216	278-329
NaOH(20)-80NaNO$_2$	230-232	206-252
NaOH(73)-27NaNO$_2$	237-238	249-295
NaOH(78.1)-3.6NaCl-18.3NaNO$_3$	242	242
NaOH(28)-72NaNO$_3$	246-247	182-257
NaOH(55.6)-4.2NaCl-40.2NaNO$_3$	247	213
LiOH(63)-37LiCl	264	437
NaOH(59)-41NaNO$_3$	266	278
LiOH(65.5)-34.5LiCl	274	339
LiOH(62)-36.5LiCl-1.5KCl	282	300
NaOH(81.5)-18.5NaNO$_3$	256-258	251-292
NaOH(59)-41NaNO$_3$	266	221
NaOH(85.8)-7.8NaCl-6.4Na2CO$_3$	282	316
NaOH(88.3)-5.3NaCl-6.4Na2CO$_3$	282	279
NaOH(87.3)-6.1NaCl-6.6Na$_2$CO$_3$	291	283
NaOH(85.8)-7.8NaCl-6.4Na$_2$CO$_3$	298	286
NaOH(77.2)-16.2NaCl-6.6Na$_2$CO$_3$	318	290
LiOH(80)-20LiF	427	1163
Nitrates		

$LiNO_3$(29)-17$NaNO_3$-	105	110
49.4KNO_3-4.6$Sr(NO_3)_2$		
$LiNO_3$(33)-67KNO_3	133	170
$LiNO_3$(31.7)-68.3KNO_3	135	136
KNO_3(53)-40NaNO2-7$NaNO_3$	142	80
$LiNO_3$(55.4)-4.5NaNO3-40.1KCl	160	266
$LiNO_3$(58.1)-41.9KCl	166	272
$LiNO_3$(47.9)-1.4LiCl-50.7$NaNO_3$	180	265
$LiNO_3$57)-43$NaNO_3$	193	248
$LiNO_3$(49)-51$NaNO_3$	194	265
$LiNO_3$(45)-47NaNO3-8$Sr(NO_3)_2$	200	199
$LiNO_3$(87)-13NaCl	208	369
KNO_3(54)-46$NaNO_3$	222	100
$NaNO_3$(54)-46KNO_3	222	117
$NaNO_3$(18.3)-3.6NaCl-78.1NaOH	242	242
$NaNO_3$(40.2)-4.2NaCl-55.6NaOH	247	213
$NaNO_3$(70)-30NaOH	247	158
$LiNO_3$(97.4)-2.6$Ba(NO_3)_2$	253	368
$LiNO_3$(93.6)-6.4NaCl	255	354
$Ca(NO_3)$2(40.85)-59.15LiCl	270	167
$NaNO_3$(86.3)-8.4NaCl-5.3Na_2SO_4	287	177

Table 1 inorganic PCM salts

2.2 Thermo physical properties of high temperature inorganic salts and salt composition

Following stage in designing and creation HSU is studying the thermo physical properties of phase change HSMs. Investigation of thermo physical properties of substances is rather labor-intensive generalizing thermo physical properties of high-temperature PCM. In 1977–1978, Marianovski and Maru with colleagues from the Chicago Institute of Gas Technology published the results of investigations of various aspects of phase change heat storage systems working above 450 ^{0}C Venkatesetti and LeFrois [5] from Honeywell, Inc. studying thermal storage materials intended for storage units in solar thermal power stations have found in the literature nine inorganic eutectic compositions with melting points between 220 and 290 ^{0}C. Thermo physical properties of nine salt mixes, measured by these authors with using a method of differential-scanning calorimetry, are presented in Table 1 Some thermal properties of salt compositions, which Birchenall and Riechman [6] found in the literature, are summarized in Table 2

Inorganic PCMs with melting temperature between 100 C and 280 C.					
Compound (wt.%)	Melting point (C)	Latent heat (kJ/kg)	Density (kg/m^3)	Energy density (kJ/m^3)	Thermal conductivity (W/m K)
$MgCl_2$ $6H_2O$	117	168.6	1450 (liquid, 120	244,470 (liquid, 120	0.570 (liquid, 120
			1569 (solid, 20	264,533 (solid, 20	0.694 (solid, 90
$NaNO_3$-KNO_3 (50:50)	220	100.7	1920	193,344	0.56
KCl-$ZnCl_2$ (68.1:31.9)	235	198	2480	491,040	0.8
LiCl-LiOH (37:67)	262	485	1550	751,750	1.10
Table 2					
Inorganic PCMs with melting temperature between 280 C and 400 C.					
Compound (wt.%)	Melting point (C)	Latent heat (kJ/kg)	Density (kg/m^3)	Energy density (kJ/m^3)	Thermal conductivity (W/m K)
$ZnCl_2$	280	75	2907	218,025	0.5
$NaNO_3$	308	199	2257	449,143	0.5
NaOH	318	165	2100	346,500	0.92
KNO_3	336	116	2110	244,760	0.5
NaCl-KCl (58:42)	360	119	2084.4	248,044	0.48
KOH	380	149.7	2044	305,987	0.5
Table 3					
Inorganic PCMs with melting temperature above 400 C.					
Compound (wt.%)	Melting point (C)	Latent heat (kJ/kg)	Density (kg/m^3)	Energy density (kJ/m^3)	Thermal conductivity (W/m K)
$MgCl_2$-NaCl (38.5:61.5)	435	351	2480	870,480	N/A
Na_2CO_3-Li2CO_3 (56:44)	496	370	2320	858,400	2.09
NaF-MgF_2 (75:25)	650	860	2820	2,425,200	1.15
$MgCl_2$	714	452	2140	967,280	0.5
LiF-CaF_2 (80.5:19.5)	767	816	2390	1,950,240	1.70 (liquid)
					3.8 (solid)
NaCl	800	492	2160	1,062,720	5.0
Na_2CO_3	854	275.7	2533	698,348	2.0
K_2CO_3	897	235.8	2290	539,982	2.0

Table 2 Available Phase Change materials at high temperatures

3. PCM container systems

Insufficient long term stability of the storage materials and containers is a problem that has limited widespread use of latent heat stores. This poor stability is due to two factors: poor stability of the material properties due to thermal cycling and corrosion between the PCM and the container. Along with attractive physical properties, the thermal storage materials should be chemically resistant and not enter chemical interaction with materials of containers, in which they are placed. This problem attracted the attention of many researchers.

3.1 Stability of the PCM container system and Corrosion of materials

A relevant aspects is the useful life of these systems and the number of cycles they can withstand without any degrading of their properties. Marianowski and colleagues [7, 8] is compatible with the stainless steel Misra and Whittenberger [9] have studied compatibility of some fluorides with constructional alloys on the basis of cobalt, iron, and nickel and of some refractory metals. In total, it has been investigated about 30 materials. The eutectic salt compositions (LIF–19.5CaF_2 with melting point 769 ^{0}C and NaF–27CaF_2–36MgF_2 with melting point 905 ^{0}C) were exposed at the temperature, which exceeded on 25 ^{0}C their melting point. The metal to be tested contacted with the salt melt placed in sealed quartz capsule or in an open crucible of alumina in the environment of argon, and was exposed from 50 till 500 h. In particular, the mild steel, pure nickel and niobium–zirconium alloy have shown resistance to all to three eutectics. Nickel alloy Hastelloy B and stainless steel SS304 have found out the minimum corrosion in contact with mix fluoride salts.

Pure metals: Pure nickel, zirconium, the titanium and silver have shown the best corrosion resistance, than various alloys on the basis of nickel, chrome and iron. Nickel has shown the least corrosion, and iron had considerable losses of metal

Alloys with the low content of chrome: Alloys on the basis of nickel and iron containing a small amount of chrome or not half containing it (Hastelloy B, Hastelloy W, and Incoloy 999) were less reactive, than alloys with the high maintenance of chrome. Alloys on the basis of zirconium and titanium: Zirconium and titanium alloys possess relatively low reactionary ability and test insignificant losses after 300 h of exposition at 500 ^{0}C

The best results have shown alloys Hastelloy N Nickel 200, Nickel 201 and stainless steels SS304, SS316. Intensity of corrosion for these alloys varied within 0.17–0.74 mm/year in for fluoride, metal hydrates salts, nitrates and nitrite salts have less or negligible corrosion per year [10]

Most references on corrosion tests using salt hydrates were performed with diluted salt hydrates as typically used in the chemical industry and only a few observation over experimental sets up. Porisini [16] tested the corrosion of four commercially available salt hydrates used as PCM in 1988. Cabeza et al [17-20 belen] studied corrosion resistance of five common metals aluminum, brass, copper, steel and stainless steel in contact with molten salts hydrates like zinc, nitrates, nitrites, hydroxides, chlorides. Recently, Gomez et al. from NREL [11] studied the corrosion of SS316 in three eutectic molten salts at around 500 ^{o}C. These salts are 80.69KNO_3 11.87KBr–7.44KCl wt. %, 60.00$MgCl_2$–20.40KCl–19. 60NaCl wt. %, and 34.81NaCl–32.29KCl–32.90LiCl wt. %. While the first salt has very low corrosion to SS316, the other two salts can have significant corrosion to SS316.

4.1 Application of high temperature thermal energy storage

Solar water-heating systems:

Cabeza et al. [12] constructed solar pilot plant at the University of Lleida to test the PCM behavior in real conditions, which could work continuously with the solar system, or could also work with an electrical heater. The PCM module geometry adopted was to use several cylinders at the top of the water tank. Several experiments with two, four and six PCM modules were carried out in the real installation. A granular PCM–graphite compound of about 90 vol. % of sodium acetate trihydrate and 10 vol. % graphite was chosen as the PCM for the experiments presented here. Author concluded that the inclusion of a PCM module in water tanks for domestic hot-water supply is a very promising technology. It would allow to have hot water for longer periods of time even without exterior energy supply, or to use smaller tanks for the same purpose. Suat et al. [13] presented a conventional open-loop passive solar water-heating system combined with sodium thiosulfate pent hydrate-phase change material (PCM) were experimentally investigated during November and then enhancement of solar thermal energy storage performance of the system by comparing with those of conventional system including no PCM was observed. Heat storage performances of the same solar water-heating system combined with the other salt hydrates-PCMs such as zinc nitrate hexahydrate, disodium hydrogen phosphate dodecahydrate, calcium chloride hexahydrate and sodium sulfate decahydrate (Glauber's salt) were examined theoretically by using meteorological data and thermo physical properties of PCMs with some assumptions. It was obtained that the storage time of hot water, the produced hot water mass and total heat accumulated in the solar water heating system having the heat storage tank combined with PCM were approximately 2.59–3.45 times of that in the conventional solar water-heating system.

Solar cookers

One of the major uses of solar energy is in cooking using different types of solar cookers. Use of these solar cookers is limited, as cooking of food is not possible in the evening. If storage of solar energy is provided in a solar cooker, than the utility and reliability of these solar cookers would increase. Few studies have been conducted with the latent heat storage materials in a box type solar cooker to cook the food in the late evening. Sharma et al. [14] developed a PCM storage unit with acetamide for a box type solar cooker to cook the food in the late evening. They recommended that the melting temperature of a PCM should be between 105 and 110 ^oC for evening cooking. Foong et al [15] testing of a small scale double-reflector solar concentrating system with heat storage. The main advantage of thermal heat storage is that the thermal energy is available also during times when there is little or no sun shine. A well-insulated heat storage should keep the heat for about 24 h. NaNO3 and KNO3 in 60:40 percent ratio (mol %) were used as latent heat storage medium. The melting temperature of about 220 ^oC is quite suitable for cooking and baking purposes. The melting of phase change material occurred within 2 to 2.5 h and reached the temperature range of 230 to 260 ^oC

Applications in power generation

TES has always been associated closely with solar installations because solar energy availability is limited, and does not coincide with energy demand periods. Nowadays there are several solar power generation plants that have TES systems To address the shortcomings of the current solar thermal energy power generation technologies and establish the usage of LHS as primary storage mechanism in solar power plants, several proposals have been developed Another energy storage proposal for solar plants, made by the German aerospace center (DRL) together with the German center for solar energy and hydrogen research (ZSW), is a combination of sensible and latent heat storage [21]. Designed for a 3 h charge time and a 1 h discharge period. The fluid used was synthetic oil and three different storage materials were used: $NaNO_3$, concrete, and a mixture of NaOH and NaCl. The most innovative aspect of this concept was the possibility of increasing the efficiency of the systems, due to the combination of the good thermal conductivity and reduced cost of concrete with the good storage characteristics of the PCM. Bruno et al[1] studied and experiment on The design of a phase change material based high temperature solar thermal energy storage device is presented. Said unit will be used as an energy reserve for a 1 kWe domestic CCHP system using a Stirling engine to produce electric power. The thermal energy storage is conducted by means of the exploitation of the latent heat of fusion of the material contained inside the tank. This method was chosen because a great energy density is obtained and, at the same time, it is possible to extract the stored energy with very small variations on the temperature, which is a favorable feature for its intended purpose. The selection of the phase change material is discussed and the design of the different components of the proposed storage model is described. It is analyzed, as well, the insulating solution applied that minimizes heat losses

4. CONCLUSIONS

Reviews a series of high temperature PCMs seeking to assist developers in the material selection being a comprehensive thermo physical properties database. The following concluding remarks can be mentioned:

- Selection of PCM mainly depends upon application and its melting point
- Stability of inorganic PCM for number of cycle should be high as possible
- Appropriate quantity and location of PCM should be determined for greater effectiveness
- For high temperature application at night it released the heat and solidifies its state
- PCM which has melting point range between 150 to 300 ^oC is mostly used in high temperature thermal energy storage like power generation, solar cooking and backing application during evening or night time
- Chloride, fluoride and nitrates salts are compatible with 304 SS and 316 SS container due to corrosive nature.

- Copper and aluminum plates or fins extended surfaces can be used to increase the heat transfer rate to PCM because inorganic PCM have low thermal conductivity

6. REFERENCES

[1] Regin AF, Solanki SC, Saini JS. Heat transfer characteristics of thermal energy\ storage system using PCM capsules: a review. Renew Sustain Energy Rev 2008; 12(9):2438–5

[2] Francis Agyenim, A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems. Renewable and Sustainable Energy Reviews 14 (2010) 615–628

[3] Lane, Low temperature heat storage with phase change materials Central Research Inorganic Laboratory

[4] Murat M. Kenisarin (2010) "High-temperature phase change materials for thermal energy storage" Renewable and Sustainable Energy Reviews 14, 955-970

[5] Venkatesetty HV, LeFrois RT. Thermal energy storage for solar power plants. In: Proceedings of 11th intersociety energy conversion engineering conference; 1976. p. 606–12

[6] Birchenall CE, Riechman AF. Heat storage in eutectic alloys. Metall Trans a 1980; 11A (8):1415–20

[7] Marianowski LG, Maru HC. Latent heat thermal energy storage systems above 450 °C. In: Proceedings of 12th intersociety energy conversion engineering conference; 1977. p. 555–66

[8] Maru HC, Dullea JF, Kardas A, Paul L, Marianowski LG, Ong E, et al. Molten salts energy storage systems. Chicago, IL: Final Report of the Institute of Gas Technology; 1978

[9] Misra AK, Whittenberger JD. Fluoride salts and container materials for thermal energy storage applications in the temperature range 973 to 1400 K. In: Paper presented at 22nd Intersociety Energy Conversion Engineering Conference (AIAA-87-9226); 1987. p.22

[10] Downing RS, Parekh MB. Thermal energy storage for an organic Rankine cycle solar dynamic powered space station. In: Proceedings of 20th intersociety energy conversion engineering conference 2; 1985. p. 397–409

[11] Trunin AC, Garkushin IK, Voronin KYu, Dibirov MA and MOshenskii YuV. Heat storage composition. USSR Patent 1089100; 1984

[12] Cabeza LF, Ibanez M, Sole C, Roca J, Nogues M. Experimentation with a water tank including a PCM module. Solar Energy Mater Solar Cells 2006; 90:1273–82

[13] Canbazoglu S, S¸ahinaslan A, Ekmekyapar A, Gokhan Aksoy Y, Akarsu F. Enhancement of solar thermal energy storage performance using sodium thiosulfate pentahydrate of a conventional solar water-heating system. Energy Build 2005; 37:235–42

[14] Sharma SD, Buddhi D, Sawhney RL, Sharma A. Design, development and performance evaluation of a latent heat unit for evening cooking in a solar cooker. Energy Convers Manage 1997; 38(5):493–8

[15] Chee Woh Foong Investigation of a small scale double-reflector solar concentrating system with high temperature heat storage Applied Thermal Engineering 31 (2011) 1807-1815

[16] F.C. Porisini, Salt hydrates used for latent heat storage: corrosion of metals and reliability of thermal performance, Solar Energy 41 (1988) 193–197

[17] L.F. Cabeza, J. Illa, J. Roca, F. Badia, H. Mehling, S. Hiebler, F. Ziegler, Immersion corrosion tests on metal salt hydrate pairs used for latent heat storage in the 32 to 36 C temperature range, Mater. Corros. 52 (2001) 140–146.

[18] L.F. Cabeza, J. Illa, J. Roca, F. Badia, H. Mehling, S. Hiebler, F. Ziegler, Middle term immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36 C temperature range, Mater. Corros. 52 (2001)748–754.
[19] L.F. Cabeza, F. Badia, J. Illa, J. Roca, H. Mehling, F. Ziegler, Corrosion experiments on salt hydrates used as phase change materials in cold storage, IEA ECES IA Annex 17 Kick-off Workshop, Lleida (Spain), 2001.

[20] L.F. Cabeza, H. Mehling, S. Hiebler, Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 48 to 58 C temperature range, Mater. Corros. In press

[21] Geyer M. Concrete thermal energy storage for parabolic trough plants. Proposal to the 5th Framework program of the European Union; 1999.

[22] Hasnain SM. Review on sustainable thermal energy storage technologies. Part I: heat storage materials and techniques. Energy Conversion Management 1998; 11:1127–38