THERMAL ENERGY STORAGES – MATERIALS AND APPLICATION

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INVITED PLENARY LECTURE

Abstract: *Thermal energy storage (TES) is a technology that gives an opportunity for using energy in the period when the production of energy is at a lower level or does not exist. TES are used when there is a mismatch between energy demand and energy supply. They increase heat generation capasity, enable better operation, increase system reliability, shift energy purchases from high to low-cost periods, they take role of expansion vessel and so on. This paper will present the field of Thermal Energy Storages (TES), methods and materials that are used as working mediums. The problems of using PCM materials as storing mediums were shown and discused. The technics for overcoming the problem of low thermal conductivity of PCM were listed and described. At the end of the article the main applications of TES were given.*

Key words: *Thermal energy storage, PCM, heat transfer enhancement,*

1. INTRODUCTION

As a result of the fact that it is impossible to use energy without environmental impact and growing energy consumption on the world, environmental problems have taken more attention in the last decades. Energy consumption permanently increases, except in 2020. when total energy consumption fell as a result of lockdown and transport restrictions caused by Covid-19 1.. The usage of energy from non-renewable sources leads to the growth of greenhouse gases emission that mainly causes global warming. Climate change and global warming significantly impact the Earth and all species and, therefore, the agriculture sector. The problems of energy use, environmental impact and environmental protection have become particularly relevant in the last decades. Hence, it is essential to improve the energy efficiency of the systems and use clean energy from renewable energy sources, including solar, biomass, wind, geothermal etc. The main problem of using renewable energy sources is that they depend on geographic locations, weather conditions and, finally, economic profitability. For example, the clean energy that the Sun emits is approximately 63 MW/m2. A tiny part of it reaches the Earth, but that energy that comes in 84 minutes would be enough to meet the world's energy needs in one year 2.. That means there is enough energy, but there are problems with catching this energy with low density and storage. The stores of any form of energy imply the accumulation of appropriate energy potential in the desired period and later use the stored form of energy for various purposes, such as performing some useful work, heating or cooling space, etc. There are different forms of energy such as kinetic, potential, chemical, nuclear, thermal (internal) energy, etc. In various systems, such as heating, cooling, air conditioning systems, etc., storing thermal energy plays an essential role in increasing energy efficiency and ensuring the safety of those systems. Devices in which the storing of thermal energy is performed are called Thermal Energy Storages or shortly TES. TES increase heat generation capasity, enable better operation, increase system reliability, shift energy purchases from high to low-cost periods, they take role of expansion vessel, etc 3.

2. THERMAL ENERGY STORAGES

TES are used in systems where there is the possibility of using waste heat from different kinds of processes and when there is a mismatch between energy demand and energy supply. Depending on the method of storing energy, TES can be classified into three types 3.:

1) Sensible - STES (the storing of energy occurs when the temperature of the storing medium, e.g. water, raises)

2) Latent – LTES (the storing of energy occurs when the storing medium changes its phase, e.g. melting, evaporation of a phase change material-PCM)

3) Thermochemical (the storing/realizing of energy occurs during chemical reactions)

Depending on the period during which storage is performed, storing of energy can be:

1) daily,

2) weekly,

3) monthly,

4) annually (seasonal).

The main characteristics of the TES are 4.:

- the amount of stored energy per unit of volume,
- the temperature range in which the storing of energy is carried out,
- heat transfer during charging and discharging processes and realized temperature differences,
- temperature layering in the TES,
- auxiliary energy for the process of charging and discharging the TES itself,
- features of the reservoir of TES and other structural elements included in the storage system,
- control of heat losses in the environment,
- price.

3. MATERIALS AND METHODS

Depending on the type of TES different materials are used as storing mediums. For sensible TES (STES) water is the most useful storing material. Water has a large heat capacity, it is in abundance, and it is not poisonous or flammable. The main disadvantages of using water as a storage material are the possibility of freezing, corrosive action and relatively low boiling temperature. In STES the storing thermal energy is based on temperature change of working medium:

$$Q = \int_{T_1}^{T_2} mc_p dT = \int_{T_1}^{T_2} \rho V c_p dT$$

where Q is the stored thermal energy, m is the mass of storing medium, c_p is the specific heat capacity of working medium at constant pressure, T_1 is the initial temperature of working medium and T_2 is final temperature of working medium, ρ is density, V is volume. The main disadvantage of using water is the fact that boiling temperature at atmospheric pressure is too low, and consequently, water is mostly used for storing thermal energy up to 100°C.

The storing of thermal energy in TES with PCM (Phase Change Material) as a working medium is primarily based on the heat of the phase change that is absorbed during the change in the phase of the working medium. For example, compared to water, applying PCM can store up to 14 times the amount of heat compared to a TES of the same volume filled by water 5.. In addition, the advantage is that the PCM changes its phase at a specific temperature or at a certain temperature range, which is also one of the important advantages given the fact that heat exchange takes place at a lower temperature difference 6..

During the phase change, the heat supplied to the working medium is used to take phase change, i.e., tearing of intermolecular ties. In addition, in most cases, the phase change processes are isobaric, and the temperature in which the phase changes can be considered constant. Therefore, the amount of thermal energy that is stored in PCM during phase change of the working medium can be determined as follows:

$$Q = m \cdot x_m \cdot r_m$$

where x_m is the mass fraction of melted/solidified PCM, m is the mass of PCM and r_m is the latent heat of fusion. However, the heating process of PCM consists of heating the PCM from the initial temperature to the melting temperature, then melting the PCM (phase change process) and heating the melted PCM to the temperature that is higher than the melting temperature. Therefore, the stored thermal energy in a PCM can be calculated as follows:

$$Q = \int_{T_1}^{T_m} mc_p dT + mr_m + \int_{T_m}^{T_2} mc_p dT$$

where T_m is the melting temperature. When the process of phase change starts at one and finish at another temperature, then the stored thermal energy can be calculated as follows

$$Q = \int_{T_1}^{T_{m1}} mc_p dT + mr_m + \int_{T_{m2}}^{T_2} mc_p dT$$

where T_{m1} is the temperature at which the melting process starts (solidus temperature), while T_{m2} is the temperature at which the melting process ends (liquidus temperature). The main advantages of STES over LTES are the lower price, simple construction, and easy manipulation, i.e. control of the heat accumulation process. The main disadvantages of this type of TES are the transient temperature difference between the temperature of the working (storing) medium and the fluid that absorbs/realize heat (Heat Transfer Fluid) 3.. Unlike STES, LTES mainly stores heat during the phase change is accompanied by a minor change in PCM because of fact that the main part of the heat is absorbed during the process of phase change 3.. That is a desirable feature of working medium because equipment and devices that are connected with a TES can work in nominal working conditions. In addition, the advantage of LTES is a greater accumulation of energy per unit of volume, i.e. per unit of mass of working medium. The stored amount of energy per unit of mass of working medium is on average 5 to 10 times higher in favour of LTES than STES 7.. Energy storage density for most available and potential PCM takes values from 90 kJ/kg up to 330 kJ/kg 8., 9.. However, despite all the advantages of LTES mentioned above comparing to STES, the application of LTES is limited by the small value of the thermal conductivity of PCM 10. 11.. Low thermal conductivity of PCM causes difficult heat transfer through PCM and thus prolongs the process of charging or discharging TES. It also leads to several undesired effects such as overheating, sub-cooling, or degradation of PCM 3..

According to their origin, all PCM can be classified into the following groups 7., 12., 13.:

1) Organic PCM,
2) Inorganic PCM.

The most used organic PCM are paraffin waxes. They are chains of *n*-alkanes with physical properties presented in Table 1.

Table 1 Thermo-physical properties of some paraffin waxes 14.

Name	Carbon atoms	Melting temperature	Density	Thermal conductivity	Latent heat of fusion
	–	°C.	kg/m^3.	W/mK.	kJ/kg.
n - Dodecane	12	-12	750	0.21^{s}	–
n - Tridecane	13	-6	756	–	–
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} 775^{L}	0.35^{s} , 0.149^{L}	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 - Tetracosane	24	51	–	–	255
n - Pentacosane	25	54	–	–	238
Paraffin wax		32	785^{s}, 749^{L}	0.514^{s}, 0.224^{l}	251
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	–	930^{s}, 830^{l}	–	–
n - Dotricontane	32	70	–	–	–

Based on Table 1. it can be concluded that there is an important difference between the thermal conductivity of solid and liquid phase of paraffin wax, but both values are too small. On the other hand as an example of inorganic PCM, hydrate salts are most often mentioned in the literature. They consist of salt and water. The water in such salts is incorporated into the crystal lattice of the salt during the curing process. Table 2 shows some of the salts used, as well as their basic thermo-physical properties. It can be concluded that salts as PCM can be used at low temperature ranges and their thermal conductivity is approximately two times larger than paraffin wax. The disadvantages of these working substances lie in the problems of salt degradation that occurs due to local sub-cooling of PCM during the solidification process, which leads to the displacement of water molecules from the salt crystal lattice. This results in a change of the thermo-physical properties of the PCM, which over time leads to a decrease in the latent heat of fusion and a reduction in others, for the heat accumulation of favourable thermo-physical properties.

Table 2 Thermo-physical properties of hydrate salts 15.

Name	Melting temperature °C.	Density kg/m³.	Thermal conductivity W/mK.	Latent heat of fusion kJ/kg.
$LiClO3 \cdot 3H2O$	8	–	–	253
$NH_4Cl \cdot Na_2SO_4 \cdot 10H_2O$	11	–	–	163
$K_2HO_4 \cdot 6H_2O$	14	–	–	108
$NaCl \cdot Na_2SO_4 \cdot 10H_2O$	18	–	–	286
$KF \cdot 4H_2O$	18	–	–	330
$K_2HO_4 \cdot 4H_2O$	18.5	1447^{20C},	–	231
$Mn(NO_3)_2 \cdot 6H_2O$	25	1738^{20C},	–	148
$LiBO_2 \cdot 8H_2O$	25.7	–	–	289
$LiNO_3 \cdot 3H_2O$	30	–	–	189-296
$Na_2SO_4 \cdot 10H_2O$	32	1485^{24C}	0.544	251-254
$Na_2CO_3 \cdot 10H_2O$	33-36	1442		247
$KFe(SO_4)_2 \cdot 12H_2O$	33	–	–	173
$CaBr_2 \cdot 6H_2O$	34	1956^{35C},	–	115-138
$LiBr \cdot 2H_2O$	34		–	124
$Na_2HPO_4 \cdot 12H_2O$	35	1522	–	256-281
$Zn(NO_3)_2 \cdot 6H_2O$	36	1828^{36C},	$0.464^{39.9C}$,	134-147
$Mn(NO_3)_2 \cdot 4H_2O$	37	–	–	115
$FeCl_3 \cdot 6H_2O$	37	–	–	223
$CaCl_2 \cdot 4H_2O$	39	–	–	158
$CoSO_4 \cdot 7H_2O$	40.7	–	–	170
$CuSO_4 \cdot 7H_2O$	40.7	–	–	171
$KF \cdot 2H_2O$	42	–	–	162-266
$MgI_2 \cdot 8H_2O$	42	–	–	133
$CaI_2 \cdot 6H_2O$	42	–	–	162
$Ca(NO_3)_2 \cdot 4H_2O$	43-47	–	–	106-140
$Zn(NO_3)_2 \cdot 4H_2O$	45	–	–	110
$K_3PO_4 \cdot 7H_2O$	45	–	–	145
$Fe(NO_3)_3 \cdot 9H_2O$	47	–	–	155-190
$Mg(NO_3)_3 \cdot 4H_2O$	47	–	–	142
$Na_2SiO_3 \cdot 5H_2O$	48	–	–	168
$Na_2HPO_4 \cdot 7H_2O$	48	–	–	135-170
$Na_2S_2O_3 \cdot 5H_2O$	48	1600		209
$K_2HPO_4 \cdot 3H_2O$	48	–	–	99
$MgSO_4 \cdot 7H_2O$	48.4	–	–	202
$Ca(NO_3)_2 \cdot 3H_2O$	51	–	–	104
$Na(NO_3)_2 \cdot 6H_2O$	53	–	–	158
$Zn(NO_3)_2 \cdot 2H_2O$	55	–	–	68
$Ni(NO_3)_2 \cdot 6H_2O$	57	–	–	168
$MnCl_2 \cdot 4H_2O$	58	–	–	151
$FeBr_3 \cdot 6H_2O$	27	–	–	105
$FeCl_3 \cdot 2H_2O$	56	–	–	90
$CO(NO_3)_2 \cdot 6H_2O$	57	–	–	115

To overcome the low thermal conductivity of the phase change materials, many authors have investigated different techniques for enhancing heat transfer. All of these techniques can be classified into the following groups 16.:

- extended surfaces-fins
- metal networks-metal foams
- composites PCM
- multiple PCM
- encapsulations

▪ *Extended surfaces-fins*

Extended surfaces are surfaces that take the role of thermal bridges that brings energy throughout a PCM. It is well known that convection is the dominant form of heat transfer during the melting or solidification process, and fins improve the lack of heat transfer by conduction. Fig.1 shown an example of inserting fins into PCM. HTF flows through the pipe located in the centre of TES 10., 11.. The heat transfer enhancement exponentially depends on the number of fins inserted into PCM. Rudonja et al. 10., 11. experimentally and numerically analyzed the influence of using rectangular copper fins on reducing the time of melting process of paraffin wax. They introduced a geometrical parameter, i.e. the surface ratio for tracking the influence of extended surfaces on melting time of PCM and consequently on heat transfer enhancement. Ahmed H.N.Al-Mudhafar et al. 17. used specially shaped fins for improving heat transfer inside the cylindrical thermal energy storages (heat exchanger). The tracking of enhanced heat transfer was done by tracking the melted mass fraction of PCM during the time and concluded that specially shaped fins were better than rectangular fins. As a working medium, RT82 was used.

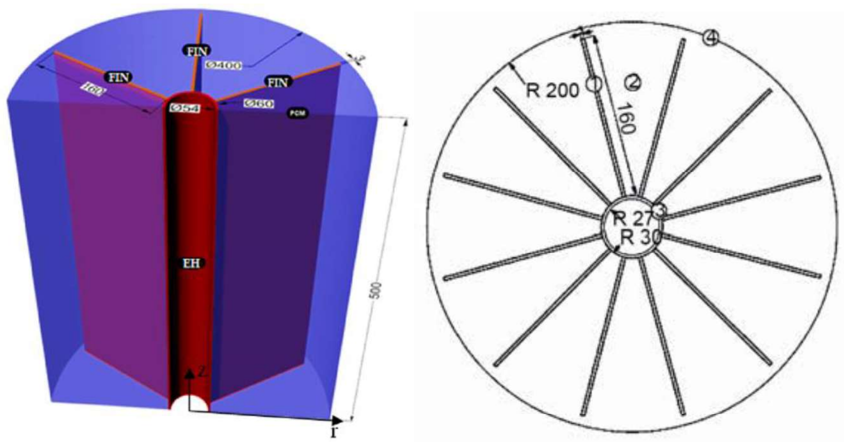

Figure 4 Extended surface-fins inserted into PCM **10. 11.**

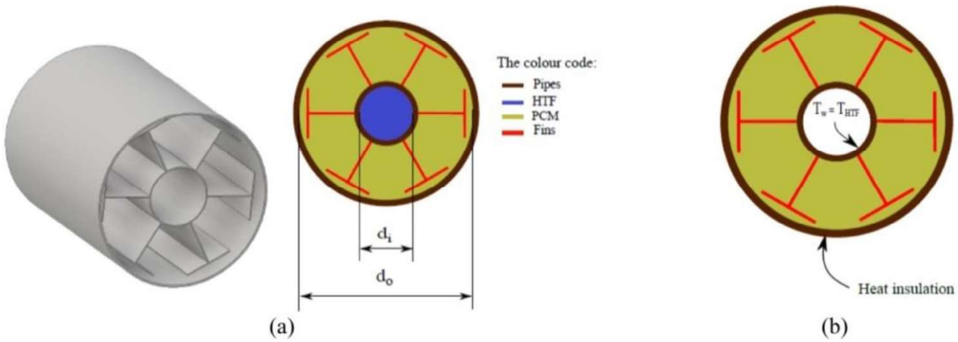

Figure 5 The physical model of TES left 3D, right the cross-sectional area, (b): the computational domain with the indicated boundary conditions for the TES with six tee fins 17.

Cláudia R.E.S.Nóbrega et al. 18. numerically and experimentally studied one axially finned tubes for cold applications. As the PCM water was used. Their results showed that increasing the number of fins and width and reducing the tube wall temperature reduces the total solidification time.

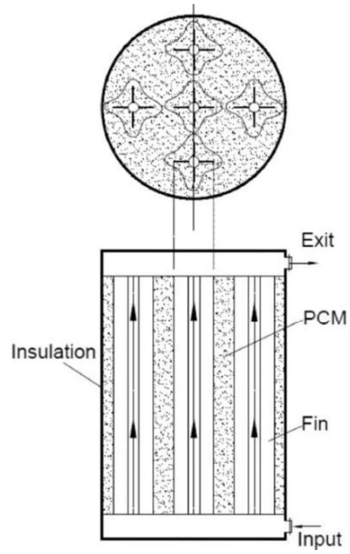

Figure 6 Simplified latent heat storage unit

- *Metal foams*

Heat transfer rate can be enhanced by using (porous) metal foams 19.. Heat transfer material is metal (copper) foam, while PCM is inserted inside foam (Fig.3). The main problem of using this enhancement technique is reducing PCM mass with increasing mass of used metal foam. Increasing the mass of metal foams leads to reduction in latent heat capacity. Hence, it is necessary to use the optimum foam mass.

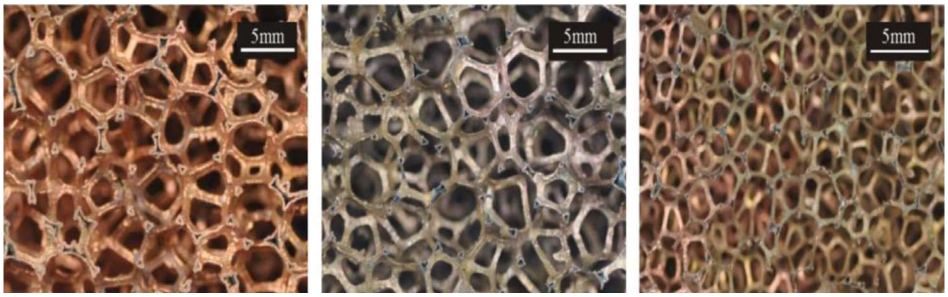

Figure 7 Copper foam samples with different pore densities and porosities 19..

- *Composites PCM*

In order to overcome the problem of low thermal conductivity into PCM are inserted materials that have a high value of thermal conductivity. Those materials are graphite, expanded perlite etc. Graphite has a high value of thermal conductivity that takes values from 24 to 470 W/(mK) 20.. Graphite used in latent heat storage materials are natural graphite flakes, expanded natural graphite, and ground expanded natural graphite (Fig.4) 21..

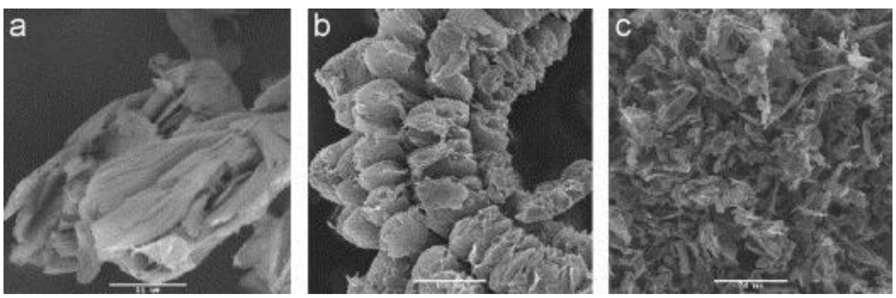

Figure 8 (a) natural graphite flakes; (b) expanded natural graphite;
(c) ground expanded natural graphite 21.

Increasing of overall thermal conductivity of a composite PCM is closely a linear function of the mass fraction of used graphite (Fig.4) 4..

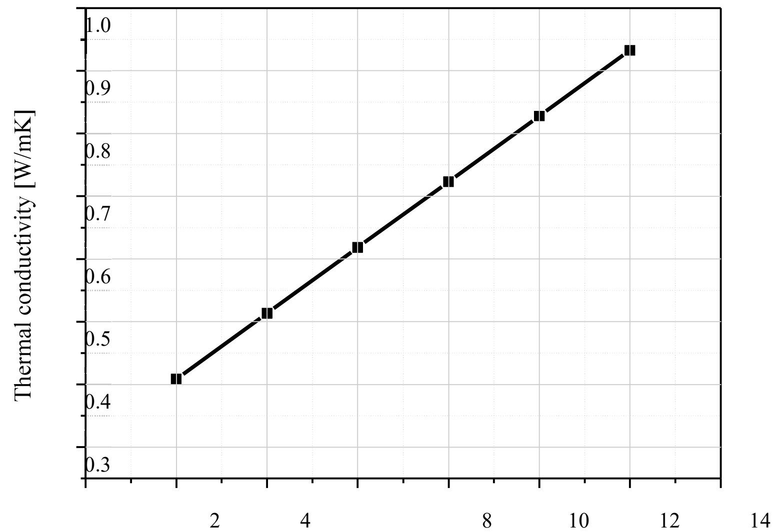

Figure 9 Thermal conductivity dependence on the mass fraction of expanded graphite 4.

- *Multiple PCM*

In this method, PCM are arranged in the way that their melting temperature decreases while the temperature of HTF also decreases 22.. In Fig. 7, it can be seen that Heat Transfer Fluid, during the charging process, flows from left to right side, and PCM are arranged so that PCM-1 has the highest melting temperature, while PCM-5 has the lowest melting temerature. HTF flows from the right to the left side during the discharging process.

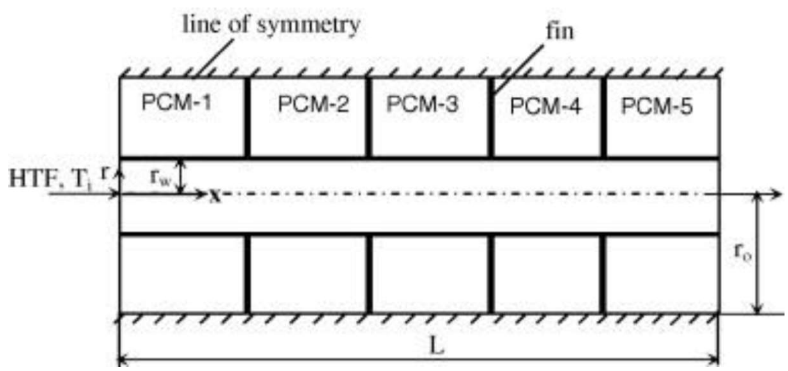

Figure 10 Schematic of the finned-tube multiple PCM LHTS unit 22.

LiangPu et al. 23. numerically investigated the heat transfer performance of shell-and-tube thermal energy storage unit consisting of multiple coaxial PCM and single PCM. They reported that utilization of a single PCM showed better heat transfer effectiveness than the use of multiple radial PCM. The results implied that the multiple radial PCM have no advantage in thermal storage compared to a single PCM. This is an important conclusion because arranging PCM in multiple thermal energy storage sometimes can produce decreasing heat transfer in TES.

- *Encapsulation*

Except for extending surfaces, another helpful method for overcoming the low thermal conductivity of PCM is encapsulation. Encapsulation increases the heat transfer surface between the PCM and the heat transfer fluid. The encapsulation can be at the micro or macro level. In micro-encapsulation of PCM micro size, PCM particles are enclosed in a sphere or cylinder. The shell can be made of the wide range of materials, including natural and synthetic polymers 24..

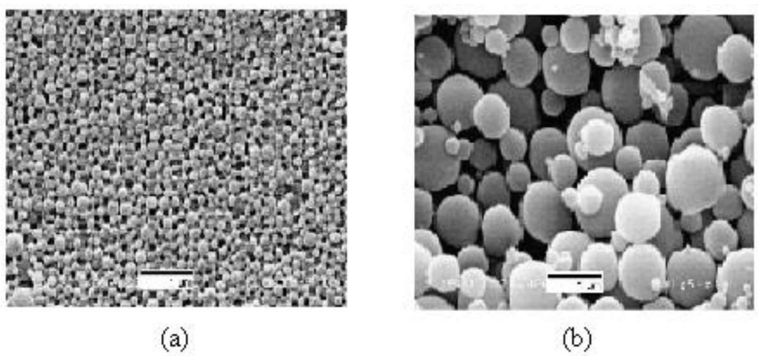

Figure 11 Microscope profiles of microencapsulated PCMs: (a) from spray-driedmicroparticles (b) from coacervation microparticles 24.

On the other hand, in macro-encapsulation PCM is inserted into metal vessels like boxes (Fig. 9), spheres (Fig. 10), panels (Fig. 11), etc. In this way, the surface of the metal shell in contact with PCM is higher and consequently, the heat transfer rate is improved.

Figure 12 Commercial rectangular macro-encapsulated PCM 25.

Figure 13 PCM encapsulated in spheres 26.

Figure 14 PCM encapsulated in metal balls 26.

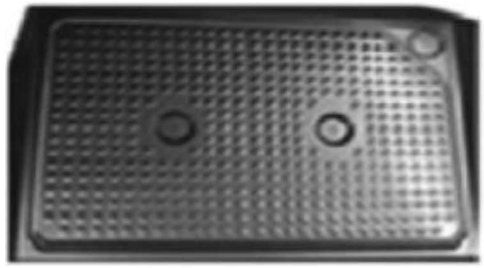

Figure 15 PCM encapsulated in aluminum panel 26.

4. APLICATION

Thermal energy storages have found a massive application in both the commercial and industrial sectors 27. 28.. TES are used in systems where there is a possibility of using waste heat from various processes 29., and then when there is a discrepancy between the need for heat and its availability, which occurs, for example, in using solar energy for heating 30. 31.. TES can also be used in cooling systems where, in conditions of reduced cooling demand, a part of the realized cooling capacity is stored, which leads to a reduction in cooling costs during subsequent use, as well as to the possibility of using refrigeration units with less power 32.– 34..

In agriculture, TES are used i.e. for the accumulation of heat obtained from combustion biomass as a part of the system for heating vegetable greenhouses 35.. A Schematic of the heating facility that was built in PKB Padinska Skela, which included TES is shown in Fig. 13 35.. In Agricultural Corporation PKB greenhouses were built for vegetable production. The specified greenhouses were covered an area of 1 ha in total. Greenhouse heating was provided via a newly 1.5 MW facility comprising a biomass boiler burning soy straw. In this manner, heavy fuel oil, previously used for greenhouse heating, was substituted by biomass, in this particular case a by-product of soy production at the PKB. TES in this system was used for storing a high quantity of energy obtained in a short period because biomass combusts fastest than other types of fuels (wood, coal). The storing material was water, while the dimension of the TES was 8 m in height and 4 m in diameter (100m^3).

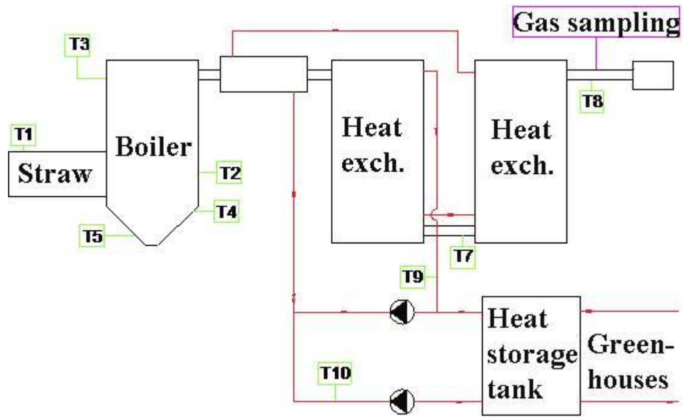

Figure 13 Schematics of the biomass burning heating system with TES 35.

Figure 16 TES in PKB Padinska Skela

The heating of greenhouses in agriculture can be directly by Sun (solar energy). However, when there is no solar energy or not enough, the heating can be realized by solar energy stored in TES. In the direct solar systems the water from the TES flows through the solar circle and there is no heat exchanger between the solar circle and the accumulation fluid. In this type of system, water in whole systems plays the role of thermal storage medium.

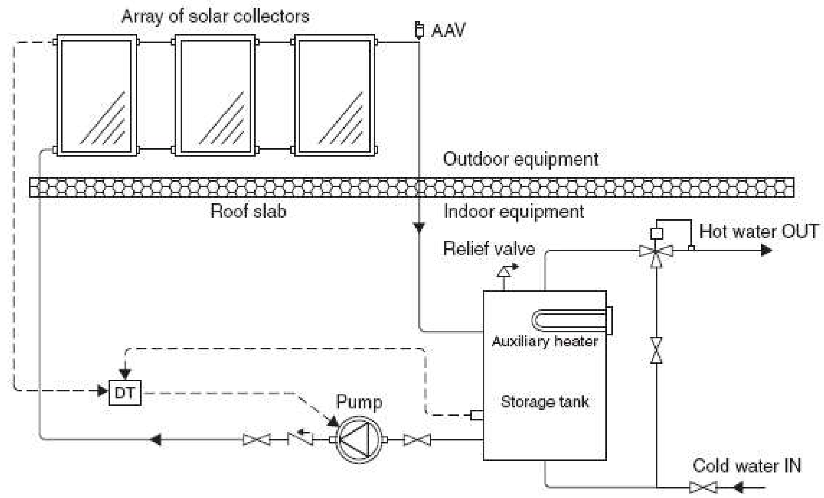

Figure 17 Direct solar water-heating system with TES 2.

If the system is indirect, then the liquid in the collector's circle does not mix with the water in the TES, the heat from the solar circle is transferred to the TES through the heat exchanger.

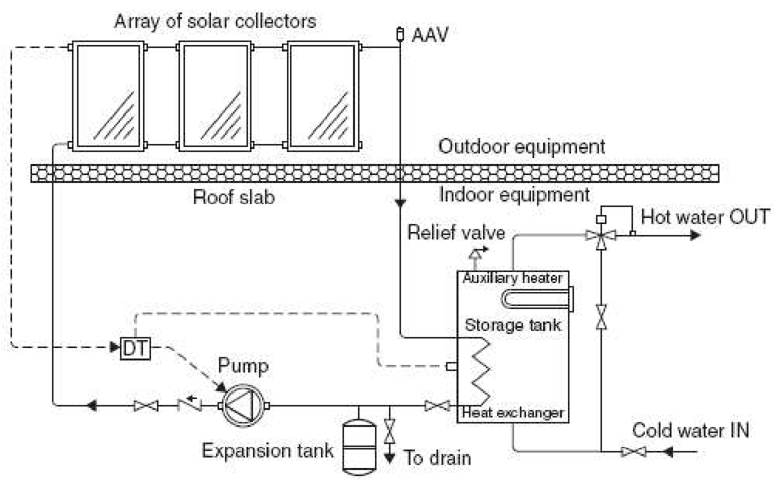

Figure 18 Indirect solar water-heating system with TES 2.

One of the most attractive applications of thermal storage is in solar thermal power plants. In those systems as working mediums are used salts. In the period of a surplus of solar energy, energy is transferred to molten salt that is pumped from cold to hot storage (Fig. 17).

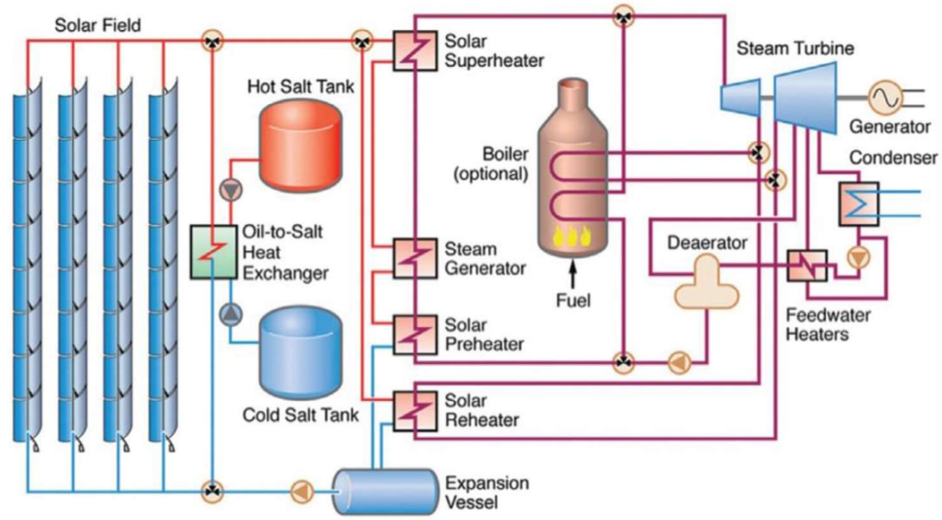

Figure 19 Parabolic trough CSP plant with indirect molten salt TES 37.

In the period when solar radiation is not sufficient, energy is transferred from melted salts to the working medium of the Rankine cycle.

Hence, the primary role of TES is storing energy. However, storing energy is not the only role of TES. For example, in the district heating systems, TES are used for pressurization of the district piping system or for acceptance of excess water due to temperature change (Fig. 18). The pressure at the connection point between the tank and the network will be determined by the level of the water surface in the tank 36..

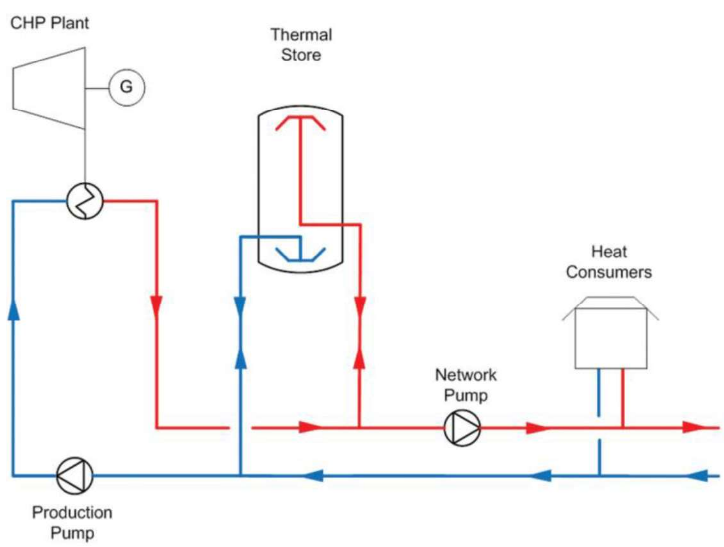

Figure 20 Thermal energy storage directly connected to a district heating network 36.

5. CONCLUSION

Thermal energy storages are an important part of any energy-efficient system. They are used for overcoming the problem of mismatch of energy supply and energy demand. They are also used in the huge district heating systems to pressurise pipeworks and as a receiver of a part of the water that appears during its temperature changes. The utilisation of working mediums is limited by temperature ranges and their own thermo-physical properties. Low thermal conductivity is a considerable problem that limits the utilisation of PCM as working mediums in TES. There are a few technics for enhancement heat transfer rate through PCM, such as extended surfaces, metal foams, composite PCM, multiple PCM and encapsulation. But, use of those enhancement methods increase investment cost and reduces latent heat capacity.

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