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Modelling of energy storage using phase-change materials (PCM materials)

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ABSTRACT

Unfortunately the global conventional fuels in reserves are running out while the world energy consumption is increasing very fast. All scientists agreed that Renewable energies is one of the best solutions for energy supply in many parts of the world.

Renewable energies are solar energy, wind energy, bio energy, geothermal energy, tidal energy, and hydropower. Approximately all these forms of energy are hampered by their high costs. Moreover, solar energy, wind energy and tidal energy are characterized by their intermittent nature, as they are not available all the time. This intermittent problem can be solved by energy storage.

Energy storage components improve the energy efficiency of systems by reducing the mismatch between supply and demand. For this purpose, phase-change materials are particularly attractive since they provide a high-energy storage density at a constant temperature which corresponds to the phase transition temperature of the material.

The aim of this thesis is to Is to describe the state of the art progress in applying PCM materials for energy storage (essentially in tanks), and opportunities of their future applications, describe physical properties of typically used PCM materials, present a mathematical model of the energy balance during the energy storage (charge) and energy discharge from the PCM material. Mathematical model is based on one-dimensional (1D) analysis.

The mathematical model consist of charging process and discharging process. During charging process the heat transfer fluid passes through the storage tank in order to transfer its thermal energy to the phase change material tube. During the discharging process, the cold water passes through the storage tank to acquire the thermal energy stored by the phase change material tube.

Different solutions utilizing PCM was assessed. It was presented different Phase Change Materials for energy storage. This assessment indicated that salt hydrates are the most energy intensive of the PCM possibilities. When we use the Paraffin for energy storage we had less energy stored then with salt hydrates used like medium for energy storage.

This assessment indicated that when we use PCM as a medium for energy storage we accumulate significantly more energy than in the case when we use water as a medium for energy storage.

There are some weaknesses in the PCM model. It was assumed that the temperature in the tank was uniform. This will not apply for the real case where the heat transfer fluid temperature will increase while transferring through the tank. For a realistic case, the temperature of the first elements will decrease rapidly because of large temperature difference between the heat transfer fluid and the PCMs in the tank.

Table of Contents

List of figures

List of tables

NOMENCLATURE

Symbol	Quantity	Units
A	Area of the PCM tube	m^2
$C_{p,water}$	Specific heat of water (HTF)	J/kgK
$C_{p,PCM,Solid}$	Specific heat of solid phase	J/kgK
$C_{p,PCM,Liquid}$	Specific heat of liquid phase	J/kgK
D_{water}	Diameter of the storage tank	m
d_{PCM}	Diameter of the PCM tube	m
d_h	Hydraulic diameter	m
h_L	Latent heat of PCM	J/kg
L	Length of storage tank	m
$m_{water,sensible}$	Mass of water sensible	kg
m_{PCM}	Mass of PCM	kg
$\dot{m}_{water,HTF}$	Mass flow rate of the water (HTF)	kg/s
$\dot{Q}$	Amount of thermal energy stored or released from sensible heta in time	J/s
T_{HTF1}	Temperature of water (HTF) at inlet	K
T_{HTF2}	Temperature of water (HTF) at outlet	K
T_{PCM}	Temperature of PCM	K
$T_{PCM,melt}$	Temperature of melting	K
T_{PCM^m}	Temperature of PCM in tim step m	K
$T_{PCM^{m+1}}$	Temperature of PCM in tim step m+1	K
Tx	Water temperature on specific place x	K

Tmean	Mean water temperatura	K
Twall	Temperature of water on wall	K
$v_{water,inlet}$	Inlet velocity of water (HTF)	m/s
V	Volume of the PCM tube	m^3
Nu	Nusselt number	-
Re	Reynolds number	-
Pr	Prandtl number	-
Δt_{in}	Initial time step	s
ρ_s	Density of solid phase	kg/m^3
ρ_L	Density of liquid phase	kg/m^3
$\rho_{water,HTF}$	Density of water (HTF)	kg/m^3
α	Heat transfer coefficient	W/m^2K
λ	Heat conduction coefficient	W/mK

Abbreviations:

PCM	Phase Change Material
HTF	Heat Transfer Fluid
TES	Thermal Energy Storage
LTES	Latent Thermal Energy Storage
SHS	Sensible heat storage
PHS	Pumped hydro storage
CAES	Compressed air energy storage
FES	Flywheel energy storage

Subscripts:

PCM	Phase change material
L	Liquid
s	Solid
w	Water
m	Index of time step

1 Introduction

Energy is the backbone of all human activities on the earth. In recent years, energy demand has increased due to the high-energy consumption in different fields. Fossil fuels have served and fulfilled all human needs from energy for long era, these fossil fuels caused huge damages for the environment that led to the most of the recent environmental problems, which are the global warming and the danger of ice melting in north and south poles. In addition, the prices of these fossil fuels increased in last years and it is expected to continue increasing in coming years because energy demand is increasing while fossil fuels in reservesare decreasing. Therefore, other sources of energy must be developed in order to take the role of fossil fuels. Renewable energies are expected to play the major role for energy supply in the near future. Renewable energies are aloso sustainable and cause much less pollution than in the case of fossile fuels. Renewable energies are solar energy, wind energy, bio energy, geothermal energy, tidal energy, and hydro-energy. Approximately all these forms of energy are hampered by their high costs. Moreover, solar energy, wind energy and tidal energy are characterized by their intermittent nature, as they are not available all the time. Another important property of these types of energy sources are strong fluctuations (on the day- or year scale), i.e. strong variations of available energy. This intermittent and fluctuation problem can be solved by energy storage.

1.1 Introduction to energy storage technology

The continuous increase in the level of greenhouse gas emissions and limited ressources of fossil fuels related to the climb in fuel prices are the main driving forces behind efforts to *more effectively* utilize various sources of renewable energy. One of the options is to develop energy storage devices, which are as important as developing new sources of energy. The storage of energy in suitable forms, which can conventionally be converted into the required form, is a present day challenge to the technologists. Energy storage not only reduces the mismatch between supply and demand but also improves the performance, efficiency and reliability of energy systems and plays an important role in conserving the energy. [1,2] It leads to saving of premium fuels and makes the system more cost effective by reducing the wastage of energy and capital cost. For example, storage would improve the performance of a power generation plant by load leveling and higher efficiency would lead to better efficiency of energy conversion and less generation cost.

List of energy storage technologies:

Mechanical storage systems

- Pumped hydro storage (PHS)
- Compressed air energy storage (CAES)
- Flywheel energy storage (FES)

Electrochemical storage systems

- Secondary batteries
- Flow batteries

Chemical energy storage

- Hydrogen
- Synthetic natural gas (SNG)

Electrical storage systems

- Double-layer capacitors (DLC)
- Superconducting magnetic energy storage (SMES)

Thermal storage systems

- Sensible heat storage
- Latent heat storage

One of prospective techniques of storing thermal energy is the application of phase change materials (PCMs). Unfortunately, prior to the large-scale practical application of this technology, it is necessary to resolve numerous problems at the research and development stage. Some of the problems are:

(i) phase separation leads to inhomogeneous material distribution, hence the performance of the heat storage changes; all properties vary in the space, and the storage process would be affected;

(ii) subcooling leads to phase change (solidification) at a lower temperature than the expected one, i.e. the temperature of melting; this simply means that the release of energy will appear at a lower temperature;

(iii) low thermal conductivity is problematic since more time is needed to achieve desired temperature level in the entire material at the same heat flux or for the time given, the temperature in the entire material will not be uniform, it will significantly vary from the heat source away.

The three main advantages of PCM for thermal energy storage are: (i) Higher thermal energy storage capacity compared to the sensible energy storage in water, (ii) relatively constant temperature during charging and discharging, (iii) burner cycles for the back-up generation unit and therefore their CO and HC emissions can be reduced.

1.2 Mechanical energy storage

Mechanical energy storage systems include:

- *gravitational energy storage* or *pumped hydropower* [1] storage (PHPS),
- *compressed air* energy storage (CAES), and
- *flywheel energy storage* (FES).

1.2.1 Pumped hydro storage (PHPS)

With over 120 GW, *pumped hydro storage* power plants represent nearly 99 % of world-wide installed storage capacity [3], which is about 3 % of global generation capacity[2]. Conventional pumped *hydro storage* systems use two water reservoirs at different elevations to pump water during off-peak hours from the lower to the upper reservoir (charging). When required, the water flows back from the upper to the lower reservoir, powering a turbine with a generator to produce electricity (discharging). There are different options for the upper and lower reservoirs, e.g. high dams can be used as pumped hydro storage plants. For the lower reservoir flooded mine shafts, other underground cavities and the open sea are also technically possible. The efficiency of PHS plants is in the range of 70 % to 85 %. Advantages are the very long lifetime and practically unlimited cycle stability of the

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[1] Strickly speaking the word *„hydroenegyy“* should be used, but in the comoon tecnical communication *„hydropower* is alredy *„established“.*

[2] The largest PHS plant in the world, with 2 100 MW peak power, is in the Bath County hydroelectric pumped storage plant located in Virginia, USA [4].

installation. Main drawbacks are the dependence on topographical conditions and large land use. The main applications are for energy management via time shift, namely non-spinning reserve and supply reserve.

1.2.2 Compressed air energy storage (CAES)

Compressed air (compressed gas) energy storage is a technology known and used since the 19th century for different industrial applications including mobile ones. Air is used as storage medium due to its availability. Electricity is used to compress air and store it in either an underground structure or an above-ground system of vessels or pipes. When needed the compressed air is mixed with natural gas, burned and expanded in a modified gas turbine. Typical underground storage options are caverns, aquifers or abandoned mines. If the heat released during compression is dissipated by cooling and not stored, the air must be reheated prior to expansion in the turbine. This process is called diabatic CAES and results in low round-trip efficiencies of less than 50 %. Diabatic technology is well-proven; the plants have a high reliability and are capable of starting without extraneous power[3]. The advantage of CAES is its large capacity; disadvantages are low round-trip efficiency and geographic limitation of locations [5].

1.2.3 Flywheel energy storage (FES)

In *flywheel energy storage* rotational energy is stored in an accelerated rotor, a massive rotating cylinder. The main components of a flywheel are the rotating body/cylinder (comprised of a rim attached to a shaft) in a compartment, the bearings and the transmission device (motor/generator mounted onto the stator[4]). The energy is maintained in the *flywheel* by keeping the rotating body at a constant speed. An increase in the speed results in a higher amount of *energy stored*. To accelerate the *flywheel electricity* is supplied by a transmission device. If the flywheel's rotational speed is reduced *electricity* may be extracted from the system by the same transmission device. Flywheels of the first generation, which have been available since about 1970, use a large steel rotating body on mechanical bearings. Advanced FES systems have rotors made of high-strength carbon filaments, suspended by magnetic bearings, and spinning at speeds from 20 000 to over 50 000 rpm in a vacuum enclosure. The main features of *flywheels* are the excellent cycle

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[3] In an adiabatic CAES process, currently under development, the released heat is retained in thermal storage (e.g. porous stones) and used again during expansion in a turbine.

[4] The stator is the static part of the assembly at the top of the tower.

stability and a long life, little maintenance, high *power* density and the use of environmentally inert material. However, *flywheels* have a high level of self-discharge due to air resistance and bearing losses and suffer from low current *efficiency*. Today flywheels are commercially deployed for *power* quality in industrial and UPS applications, mainly in a hybrid configuration. Efforts are being made to optimize *flywheels* for long-duration operation (up to several hours) as power storage devices for use in vehicles and power plants.

In the Figure 1 it is shown exemple Beacon POWER Flywheel energy storage system. Flywheel energy storage works by accelerating a cylindrical assembly called a rotor (flywheel) to a very high speed and maintaining the energy in the system as rotational energy. The energy is converted back by slowing down the flywheel. The flywheel system itself is a kinetic, or mechanical battery, spinning at very high speeds to store energy that is instantly available when needed. At the core of Beacon's flywheel is a carbon-fiber composite rim, supported by a material hub and shaft and with a motor/generator mounted on the shaft. Together the rim, hub, shaft and motor/generator assembly from the rotor. When charging (or absorbing) energy, the flywheel's motor acts like a load and draws power from the grid to accelerate the rotor to higher speed. When discharging, the motor is switched into generator mode, and the inertial energy of the rotor drives the generator the generator which, in turn, creates electricity that is than injected back into the grid [6]. Adventages of this system are:

- High performance: Less regulation needs to be purchased. Existing resources can operate more efficiently. Enhances renewable integration.
- High cycle life: 100,000 equivalent full charge/discharge cycles over a 20 year design life.
- No degradation: Energy storage capacity and performance does not degrade with cycle duty, depth of discharge, charging rate, time or temperature.
- Flexible: Capable of charging as fast as it discharges and switching power direction almost instantaneously.
- No direct air emissions, no air permits or water use. NEPA evaluation: “Findings of No Significant Impact”

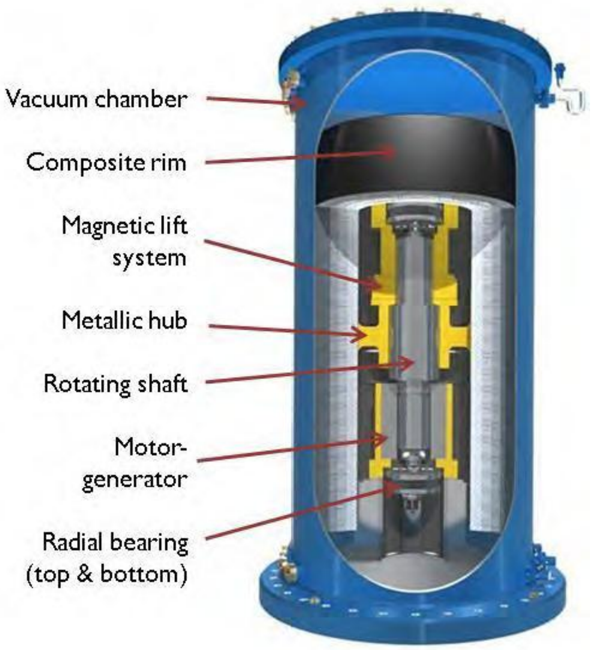

Figure 1: Beacon POWER Flywheel energy storage system [6]

1.3 Electrical 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*, whereby the *electrical energy* is converted into chemical one. When the battery is discharged, the stored *chemical energy* is converted into *electrical energy*. Potential applications of batteries are utilization of *off-peak power*, *load leveling*, and *storage of electrical energy* generated by wind turbines or photovoltaic plants. The most common type of storage batteries is the lead acid and Ni–Cd.

1.3.1 Lead acid battery (LA)

Lead acid batteries are the world’s most widely used battery type and have been commercially deployed since about 1890. Lead acid battery systems are used in both mobile and stationary applications. Their typical applications are emergency power supply systems, stand-alone systems with PV, battery systems for mitigation of output fluctuations from wind power and as starter batteries in vehicles. In the past, early in the “electrification age” (1910 to 1945), many lead acid batteries were used for storage in grids. Stationary lead acid batteries have to meet far higher product quality standards than starter batteries. Typical service life is 6 to 15 years with a cycle life of 1 500 cycles at 80 % depth of discharge, and they achieve cycle efficiency levels of around 80 % to 90 %. Lead acid batteries offer a mature and well-researched technology at low cost. There are many types of lead acid batteries available, e.g. vented and sealed housing versions (called valve-regulated lead acid batteries, VRLA). Costs for stationary batteries are currently far higher than for starter batteries. Mass production of lead acid batteries for stationary systems may lead to a price reduction. One disadvantage of lead acid batteries is usable capacity decrease when high power is discharged. For example, if a battery is discharged in one hour, only about 50 % to 70 % of the rated capacity is available. Other drawbacks are lower energy density and the use of lead, a hazardous material prohibited or restricted in various jurisdictions. Advantages are a favourable cost/performance ratio, easy recyclability and a simple charging technology. Current R&D on lead acid batteries is trying to improve their behaviour for micro-hybrid electric vehicles [7,8].

1.3.2 Nickel Cadium (NiCd) batteries

Nickel cadmium (NiCd) batteries had been in commercial use since about 1915. Compared to lead acid batteries, nickel-based batteries have a higher power density, a slightly greater energy density and the number of cycles is higher; many sealed construction types are available. From a technical point of view, NiCd batteries are a very successful battery product; in particular, these are the only batteries capable of performing well even at low temperatures in the range from -20 °C to -40 °C. Large battery systems using vented NiCd batteries operate on a scale similar to lead acid batteries. However, because of the toxicity of cadmium, these batteries are presently used only for stationary applications in Europe. **Since 2006 they have been prohibited for consumer use** [9,10,11].

1.3.3 Lithium ion battery (Li-ion)

Lithium ion batteries have become the most important storage technology in the areas of portable and mobile applications (e.g. laptop, cell phone, electric bicycle, electric car) since around 2000. High cell voltage levels of up to 3.7 nominal Volts mean that the number of cells in series with the associated connections and electronics can be reduced to obtain the target voltage. For example, one lithium ion cell can replace three NiCd or NiMH cells which have a cell voltage of only 1.2 Volts. Another advantage of Li-ion batteries is their high gravimetric energy density, and the prospect of large cost reductions through mass production. Although Li-ion batteries have a share of over 50 % in the small portable devices market, there are still some challenges for developing Lithium ion batteries generally have a very high efficiency, typically in the range of 95 % - 98 %. Safety is a serious issue in lithium ion battery technology. Most of the metal oxide electrodes are thermally unstable and can decompose at elevated temperatures, releasing oxygen which can lead to a thermal runaway. To minimize this risk, lithium ion batteries are equipped with a monitoring unit to avoid over-charging and over-discharging. Usually a voltage balance circuit is also installed to monitor the voltage level of each individual cell and prevent voltage deviations among them. Lithium ion battery technology is still developing, and there is considerable potential for further progress. Research is focused on the development of cathode materials [12,13].

1.4 Thermal energy storage

Thermal energy storage through PCM is capable of storing and releasing larg amounts of energy. The system depends on the shift in phase of the material for holding and releasing the energy. For instance, processes such as melting, solidifying or evaporation require energy. Heat is absorbed or released when the material changes from solid to liquid and vice versa. Therefore, PCMs readily and predicatably change their phase with a certain input of energy and release this energy at a later time. PCM depends on latent heat storage. Compared to the storage of sensible heat, there is no temperature change in the storage. In a sense every material is a phase change material, because at certain combinations of pressure and temperature every material can change aggregate state (solid, liquid, gaseous). In a change of aggregate state, a large amount of energy, the so-colled latent heat can be stored or released at an almost constant temperature. Thus a small difference in temperature can be used for storing energy and releasing the stored energy

Thermal energy storage can be stored as a change in internal energy of a material as *sensible heat*, *latent heat* and *thermochemical* or *combination of these*. An overview of major techniques of storage of thermal energy is shown in Fig. 2 [14]

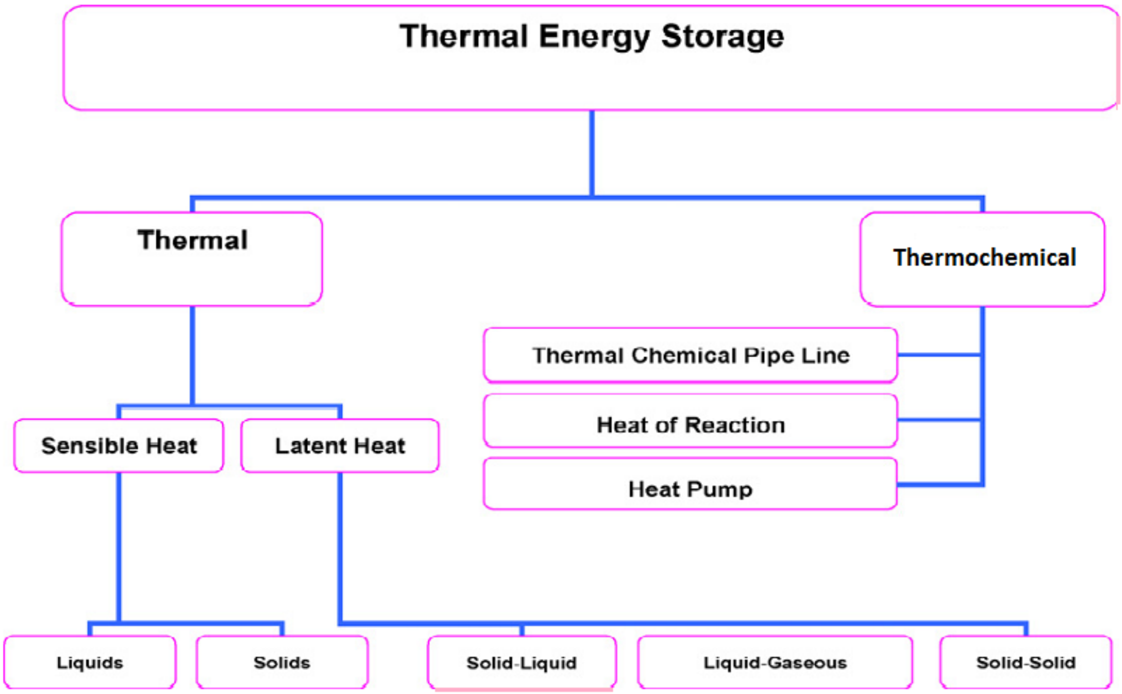

Figure 2: Different types of termal storage of solar energy [14]

1.4.1 Sensible heat storage

In sensible heat storage (SHS), thermal energy is stored by raising the temperature of a material, practically a solid or liquid. SHS system utilizes the heat capacity and the change in temperature of the material during the process of charging and discharging. The amount of heat stored depends on the specific heat of the medium, the temperature change and the amount of storage material [15].

As fig.3 shows, heat transferred to the storage medium leads to a temperature increase of the storage medium. A sensor can detect this temperature increase and the heat stored is thus called sensible heat [16].

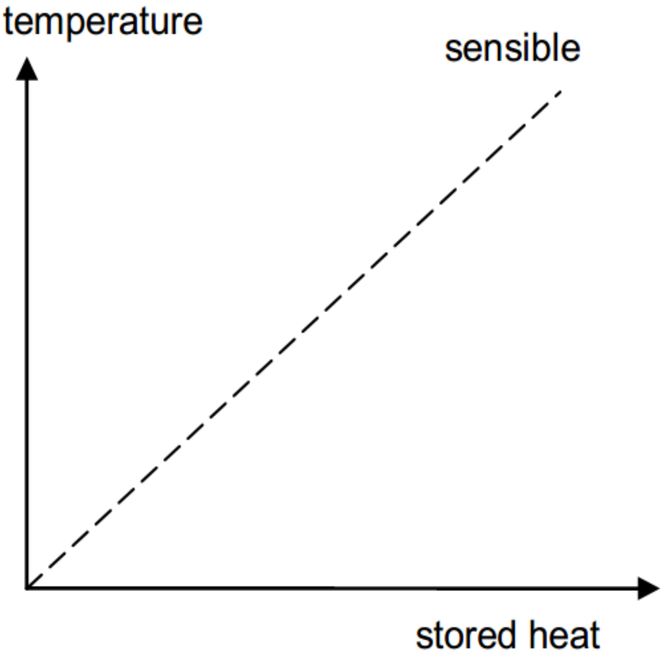

Figure 3: Heat storage as sensibile heat leads to a temperature increase when heat is stored [16]

Often the heat capacity is given with respect to the amount of material, the volume, or the mass. It is then called molar, volumetric, or mass specific heat capacity and denoted by *c*. Eq.1 shows the case of the mass specific heat capacity were *m* is the mass of the storage material.

$$Q = \int_{T_i}^{T_f} m \cdot c_p \cdot dT \tag{1}$$

$$Q = m \cdot c_p \cdot (T_f - T_i) \tag{2}$$

Where: Q is the amount of thermal energy stored or releasedin form of sensible heat (kJ), T_i is the initial temperature (°C), T_f is the final temperature (°C), m is the mass of material used to store thermal energy (kg), and Cp is the specific heat of the material used to store thermal energy (kJ/kg°C).

Sensible heat storage is often used with solids like *stone* or *brick*, or liquids like *water*, as storage material. Gases have very low volumetric heat capacity and are therefore not used for sensible heat (or *cold*) storage. The sensible heat storage capacity of some selected solid and liquid materials is shown in Table 1. *Water appears to be the best SHS liquid available because it is inexpensive and has a high specific heat*. However above 100˚C (i.e. above the boiling point, which is pressure and temperature dependent), the steam has relatively low heat capacity. Hence, oils, molten salts and liquid metals, etc. are used for the temperatures above the boiling point. For air heating applications rock-bed type storage materials are used [16].

Table 1: A list of selected solid – liquid materials for sensible heat storag

Material	Fluid type	Temperature range °C	Density (kg/m³)	Specific heat (J/kg K)
Rock	Solid	20	2560	879
Brick	Solid	20	1600	840
Concrete	solid	20	1900-2300	880
Water	Liquid	0-100	1000	4190
Caloriea HT43	Liquid (Oil)	12-260	867	2200
Engine oil	liquid	Up to 160	888	1880
Ethanol	Organic liquid	Up to 78	790	2400
Proponal	Organic liquid	Up to 97	800	2500
Butanol	Organic liquid	Up to 118	809	2400
Isotunaol	Organic liquid	Up to 100	808	3000
Isopentanol	Organic liquid	Up to 148	831	2200
Octane	Organic liquid	Up to 126	704	2400

1.4.2 Latent heat storage

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 [17] is given by:

$$Q = \int_{Ti}^{Tm} m \cdot c_p \cdot dT + m \cdot a_m \cdot \Delta h_m + \int_{Tm}^{Tf} m \cdot c_p \cdot dT \qquad (3)$$

or in a simplified form:

$$Q = m\left[c_{sp}\left(T_m - T_i\right) + a_m \cdot \Delta h_m + c_{lp}\left(T_f - T_m\right)\right] \tag{4}$$

The first term represents the heat transfer from the heat storage to the heat transferring fluid before the PCM slidificates. The second term represents the energy released during phase change and the last term represents the sensible energy transferred from the solid PCM to the heat transferring fluid.

Where: Q is the amount of thermal energy stored or releasedin form of sensible heat (kJ), T_i is the initial temperature (°C), T_m (°C) is the melting temperature (°C), T_f (°C) is the final temperature, m (kg) is the mass of heat storage medium (kg), c_p (kJ/kg°C) is the specific heat (kJ/kg°C), a_m is the fraction melted (-) and, Δh_m is the heat of fusion per unit mass (kJ/kg).

1.4.2.1 Latent heat of solid – liquid phase change

There are several options of energy storage with solid – liquid phase chaneg with distinct advantages and disadvantages. As compared to sensible heat storage, the phase change by melting and solidification can store large amounts of heat or cold, if a suitable material is selected. *Melting is characterized by a small volume change*, usually less than 10%. If a container can fit the phase with the larger volume, usually the liquid, the pressure is not changed significantly and consequently melting and solidification of the storage material proceed at a constant temperature. Upon melting, while heat is transferred to the storage material, the material still keeps its temperature constant at the melting temperature, also called phase change temperature [18] (fig.4).

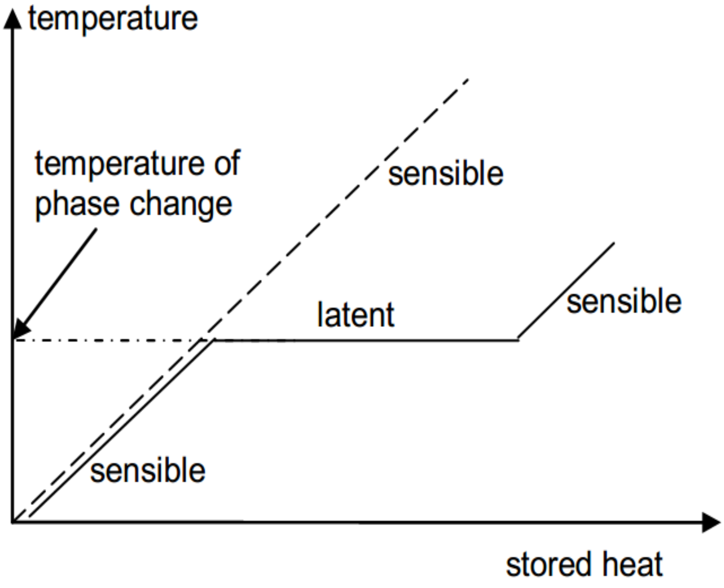

Figure 4: Heat storage as latent heat for the case of solid – liquid phase change [18]

When the melting is completed, further transfer of heat results in additional sensible heat storage. The storage of the heat of melting can not be detected from the temperature, because the melting proceeds at a constant temperature. The heat supplied upon melting is therefore called latent heat, and the process latent heat storage (LHS). Because of the small volume change, the stored heat is equal to the enthalpy difference.

$$\Delta Q = \Delta H = m \cdot \Delta h \tag{5}$$

Where; ΔQ=ΔH is enthalpy difference between the solid and the liquid phase (kJ), m is the mass of heat storage medium (kg), Δh is the change in enthalpy during the phase change (kJ/kg).

The latent heat, that is the heat stored during the phase change process, is then calculated from the enthalpy difference ΔH between the solid and the liquid phase. In the case of solid-liquid phase change, it is called solid-liquid phase change enthalpy, melting enthalpy, or heat of fusion. Materials with a solid-liquid phase change, which are suitable for heat or cold storage, are commonly referred to as latent heat storage material or simply phase change material (PCM).

1.4.2.2 Latent heat of liquid – vapor phase change

The liquid-vapor phase change by evaporation and condensation also usually has a large phase change enthalpy; however, the process of evaporation strongly depends on the boundary conditions:

- **In closed systems with constant volume**, evaporation leads to a large *increase of the vapor pressure*. A consequence of the rising vapor pressure is that the temperature necessary for a further phase change also rises. Liquid-vapor phase change in a constant volume is therefore usually *not useful* for heat storage.
- **In closed systems at constant pressure**, evaporation leads to *a large volume change*. This is *difficult to realize* and thus also not applied for heat storage.
- **Open systems at constant**, that means ambient **pressure**, are a third option. This option avoids a change of the phase change temperature. Upon loading the storage with heat, the storage material is evaporated. Because the system is open, the storage material is lost to the environment. To retrieve the stored heat from the storage, the storage material has to be retrieved from the environment. This means it has to be a natural part of the environment. The only technically used material today is *water*.

If only one component is present, like water, the process is specifically called *homogeneous* evaporation-condensation. Water however does not condense at a high rate from the atmosphere by itself. Therefore, *the condensation must be improved by a reduction of the water vapor pressure in the storage using a hygroscopic surface*. The hygroscopic effect can be caused by the adsorption of the water at the surface of a solid or the absorption in a liquid (fig.5). Due to the second component, this is called *heterogeneous* evaporation-condensation.

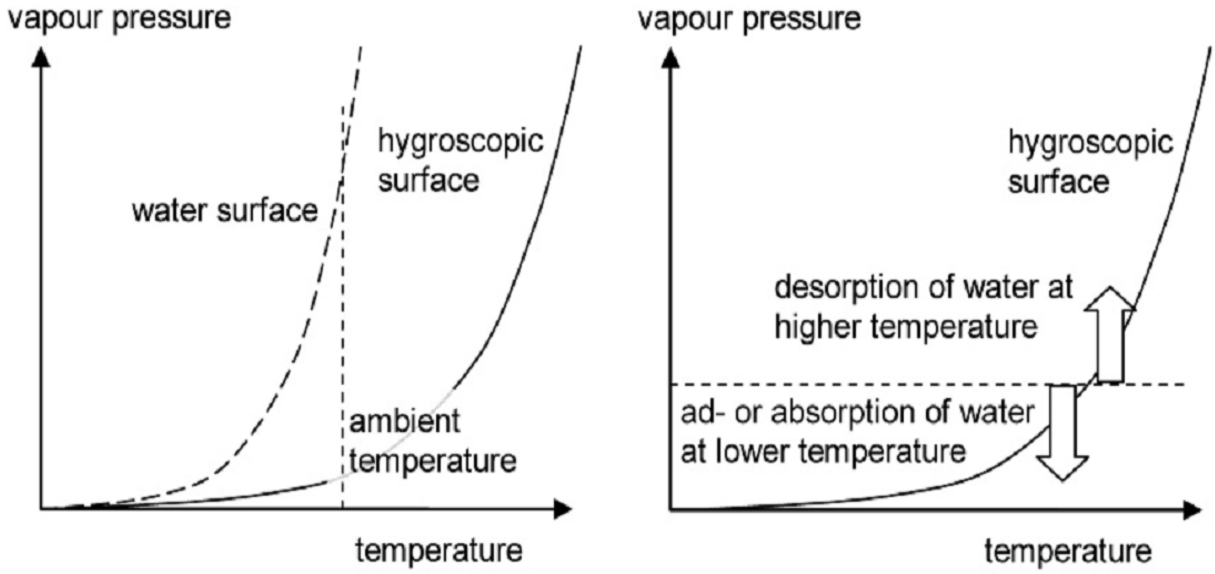

Figure 5: Change of water vapor pressure a a function of temperature using a hygroscopic surface (left) and the application of this effect for heat storage (right) [18]

When water is absorbed in a liquid, usually a salt solution that is strongly hygroscopic at ambient temperature is used. In a first step, the salt solution will absorb water from the atmosphere and the heat of solution and the heat of condensation are released (fig.5). While absorbing water the salt solution is diluted. In a second step, the water can be released (desorbed) again by supplying heat to the salt solution and thereby storing the heat in the salt solution. While desorbing water, the concentration of the salt solution rises again to the level at the beginning. The same effect is used in ad - and desorption on solid surfaces. Instead of having a hygroscopic liquid, the water is here adsorbed at the surface of micro pores in a highly porous solid like zeolite. Because of the additional energetic effect due to the solution of the vapor in the liquid or the adsorption at the surface, *the total enthalpy change in a heterogeneous evaporation or condensation is higher than for the corresponding homogeneous evaporation or condensation*. The amount of heat stored when using ad - and desorption can be calculated with Eq.5 using the appropriate enthalpy change. The process of adsorption and desorption, that is the heat release and heat storage proceed at different temperatures, as shown in fig.5. This is a significant difference to solid-liquid phase changes [18].

1.5 Thermochemical energy storage

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

$$Q = a_r \cdot m \cdot \Delta h_r \qquad (6)$$

Where: Q is the amount of thermal energy stored or releasedin form chemical reaction (kJ), m (kg) is the mass of heat storage medium (kg), a_r is the fraction melted (-) and, Δh_r is the heat of fusion per unit mass (kJ/kg).

When a chemical reaction takes places, there is a difference between the *enthalpy* of the substances present at the end of the reaction and the *enthalpy* of the substances at the start of the reaction. This enthalpy difference is known as heat of reaction. If the reaction is endothermic, it will absorb this heat while it takes place; if the reaction is exothermic, it will release this heat. Any chemical reaction with high heat of reaction can be used for thermal energy storage if the products of the reaction can be stored and if the heat stored during the reaction can be released when the reverse reaction takes place. If all components involved in the chemical reaction are solid or liquid the necessary storage space iscomparatively small. If any of the components is a gas, the same restrictions apply as for liquid-vapor phase changes. A possible solution is to use the oxidation and reduction of chemi-cals with oxygen O_2, as oxygen is easily available from the ambient air. The amount of heat stored when using chemical reactions can be calculated with eq.1.6, using the appropriate enthalpy change. As the binding energy in a chemical reaction is usually large, the temperature necessary to destroy the bond is usually high.

2 List of energy storage projects

This is a list of large energy storage projects around the globe. Many of the individual energy storage projects are designed to augment the world's electrical grids by capturing excess electrical energy during periods of low demand and storing it in other forms until needed on the grid. At that time the energy is converted back to its electrical form and returned to the grid [19].

Another energy storage method is the consumption of surplus or low-cost energy (typically during night time) for conversion into resources such as hot water, cool water or ice, which is then used for heating or cooling at other times when electricity is in higher demand and at greater cost per kilowatt hour (kWh). Such thermal energy storage is often employed at end user sites such as large buildings, and also as part of district heating thus 'shifting' energy consumption to other times for better balancing of supply and demand [19].

Table 2: List of larges energy storage project

Name	Type	Rated MW x hours	Description	Location
Bath County Pumped Storage Station	Pumped Hydro Storage Open Loop	3.030x10,3	This project consist of a 3GW Pumped Hydro Storage plant in Virginia that pumps water to an elevated reservoir at night and lets it run back down to generate electricity durning the day.	George Washington National Forest, Warm Springs Virginia United States
Advanced Underground CAES project With Saline Porous Rock Formation	Compressed Air Storage, In-ground	300x10	A 300MW A-CAES demo plant will use an underground storage container (depleted gas reservoir) and next generation turbomachinery. The project has 3 phases: Phase 1 - preliminary engineering, geologic reservoir engineering, economic analyses, and regulatory permitting; Phase 2 - Construction and plant commissioning; Phase 3 - Plant operation and plant performance monitoring. Phase 2 of the project will go ahead if the Phase 1 results show PG&E and California regulatory management that the project is cost effective.	Kern County, California United States

Notrees Wind Energy Storage Project	Battery, Advanced Lead Acid	36x0,25	Duke Energy is deploying a wind energy storage demonstration project et the Notrees Wind power project in wester Texas. The project will demonstrate how energy storage and power storage technologies can help wind power systems address intermittency issues by building a 36MW turnkey energy storage and power menagment system capable of optimizing the delivery of energy, in addition to providing regulation service in the ERCOT market.	Notrees, Texas United State
Laurel Mountain	Battery, Lithium Ion	32x0,25	The AES corporation has installed a wind generation plant consisting of 98 MW of wind generation and 32 MW of integrated battery-based energy storage. The project is supplying emissions-free renewable energy and clean, flexible, operating reserve capacity to the PJM Interconnection, the largest power market in the world.	Elkins, West Virginia, United States
Redding Electric Utilities - Peak Capacity, Demand Response, HVAC Replacment Program Phase 2	Thermal storage, Ice	6x2,0	Ice Energy and REU will collaborate on the second phase. The program to install Ice Bear Units withen the northen California territory aims to reduce peak electricity load demand by up to 6 MW over five years. REU expecet to have the thermal energy storage program completed in 2017. Skyway Machine, a local Redding manufacturing company, will provide final assembly of the new Ice Bear Units.	Redding, California, United States
University of Central Florida	Thermal Storage, Chilled Water	3x8,0	Chilled Water thermal energy storage system that is integrated into the existing district cooling system for university.	Orlando, Florida, United States
Beacon New York Flywheel Energy Storage Plant	Flywheel	20x0,25	Bacon installed a 20MW flywheel plant used for frequency regulation in the NYISO service area. The project is the largest flywheel installaton in the world and consists of 200 individual spinning masses.	Stephentown, New York, United States

3 State of the art of thermal energy storage

Amongst thermal heat storage techniques described in Sec. 1.4, *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 phase change material (PCM). Phase change can be in the following form: solid–solid, solid–liquid, solid–gas, liquid–gas and vice versa.

3.1 Phase transformations

In *solid–solid* transitions, heat is stored as the material is transformed from one crystalline to another. These transitions generally have *small*er *latent heat* and *small*er *volume changes* than solid–liquid transitions. Solid–solid PCMs offer the advantages of less stringent container requirements and greater design flexibility [20]. Most promising materials for solid-solid phase chang are organic solid solution listed in Table 3. [21]

Table 3: List of most promising materials for solid-solid phase change

Materials	Melting temperature (°C)	Latent heat of fusion (kJ/kg)
Pentaerythritol	1888	323
Pentaglycerine	818	216
Li_2SO_4	578	214
KHF_2	1968	135

Solid–gas and *liquid–gas* transition have *higher latent heat of phase transition*, but their *large volume changes* on phase transition at (nearly) constant pressure are associated with the containment problems and rule out their potential utility in thermal-storage systems. Large changes in volume make the system complex and impractical [22].

Solid–liquid transformations have comparatively *smaller latent heat than liquid–gas*. However, these transformations involve only a *small change in volume* (of order of 10% or less). Hence, solid–liquid transitions have proved to be economically attractive for use in thermal energy storage systems. PCMs themselves cannot be used as heat transfer medium. A separate heat transfer medium must be employed with heat exchanger in between to transfer energy from the source to the PCM and from the PCM to the load. The most widely used heat transfer fluid in solar hot water systems is pure water. Many different fluids have been tried over the years. Propylene glycol-water mix, ethylene glycol-water mix, synthetic oil and silicone oil are some examples. Of the ones mentioned, only propylene glycol water mix is considered acceptable. Ethylene glycol is toxic and should not be used in applications where people could be exposed to it. It will also deteriorate and damage pipes, coupling and clamps in a system. The oils will require specialized components since it will dissolve all rubber and plastic components and seals. Oils are also poor in terms of heat capacity and heat transfer [23].

Propylene glycol-water mix is in many ways considered the standard heat transfer fluid of the industry [23]. The reason to resort to propylene glycol-water mix instead of pure water is in order to prevent the liquid from freezing solid andbursting the pipes. In all other aspects, water is by far the superior heat transfer fluid. One of the most important advantages is that it has high specific heat capacity as well as high thermal conductivity. This makes it a very descent fluid for storing and transferring thermal energy. It is also inexpensive, easily attainable and its properties will not alter or change over time [24].

Propylene glycol-water mix, though essentially non-toxic, can still cause deterioration and damaging of the system. Over time it will lose and alter its properties. As this happen it will become more acidic and its antifreeze properties will wear out. It is therefore important to check the heat transfer fluid periodically in orderto ensure a pH-value above 7.5 [23]. Increased need of maintenance makes for higher operating costs for the system compared to those based on pure water.

Any latent heat energy storage system therefore, possess at least following three components:

- 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.

The development of a latent heat thermal energy storage system hence, involves the understanding of three essential subjects: *phase change materials*, *containers materials* and *heat exchangers*. A wide range of technical options available for storing low temperature thermal energy is shown in Fig. 6 [22].

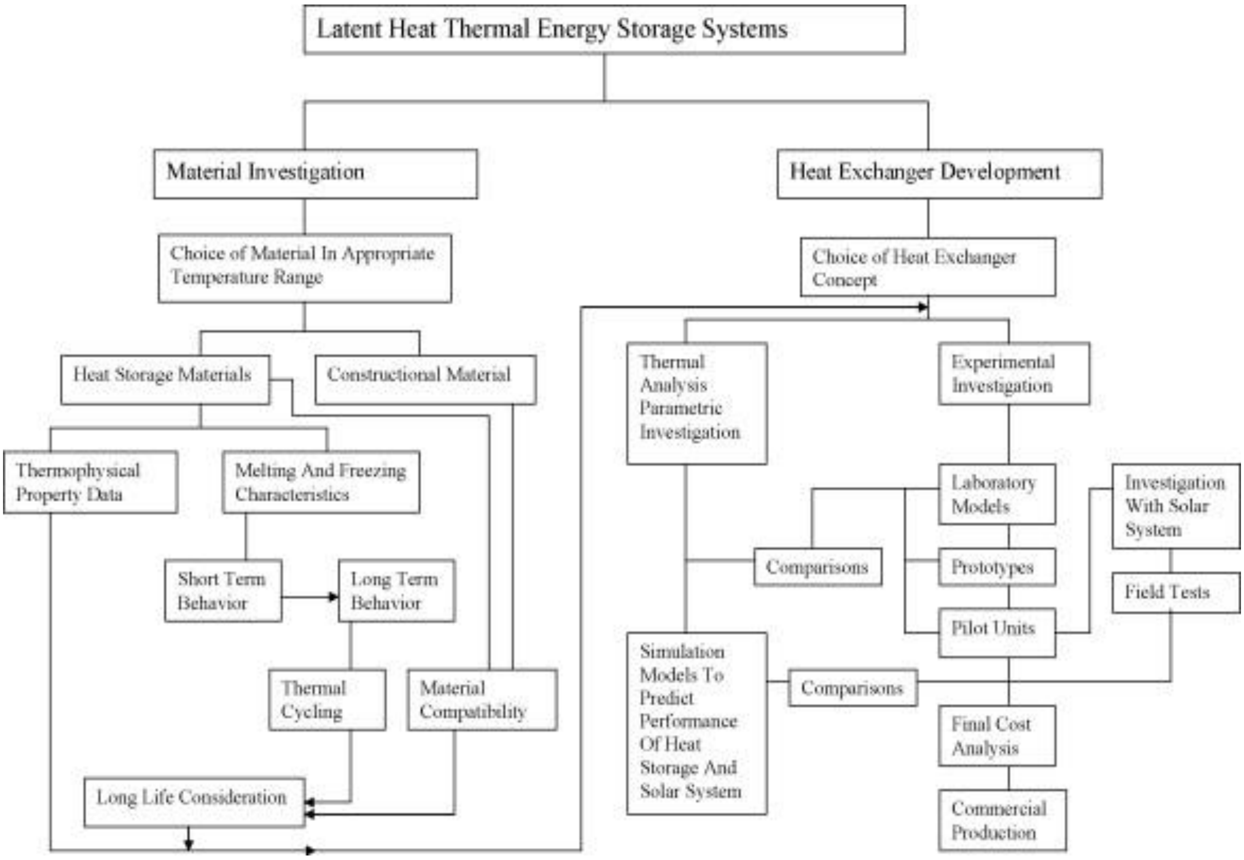

Figure 6: Flow chart showing. different stages involved in the development of latent heat storage system [22].

3.2 Different thermal energy storage technologies

3.2.1 Solar water-heating systems

Solar water heaters are getting popularity [25,26] since they are relatively inexpensive and simple to fabricate and maintain.

Prakesh et al. [27] analyzed a built-in storage type water heater containing a layer of PCM filled at the bottom. During the sunshine hours, the water gets heated up which in turn transfers heat to the PCM below it. The PCM collects energy in the form of latent heat and melts. During off 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 on changing its phases from liquid to solid. This type of system may not be effective due to the poor heat transfer between PCM and water.

Study of solar energy storage systems based on the latent heat and sensible heat technique has been carried out to preserve the solar heated hot water for night duration by Chaurasia et al. [28]. For this purpose, two identical storage units were used. One storage unit contained 17.5 kg paraffin wax (melting point about 54 °C) as the storage material packed in a heat exchanger made of the aluminum tubes and another unit simply contained the water as a storage material in a GI tank. Both units were wax. The collector's effective area was assumed to be 1 m^2 and its total volume was divided into five sectors. The experimental apparatus was designed to simulate one of the collector's sectors, with an apparatus absorber effective area of 0.2 m^2. Outdoor experiments were carried out to demonstrate the applicability of using a compact solar collector for water heating. The time-wise temperatures of the PCM were recorded during the processes of charging and discharging. The solar intensity was recorded during the charging process. Experiments were conducted for different water flow rates of 8.3 – 21.7 kg/h. The effect of the water flow rate on the useful heat gain was studied. The heat transfer coefficients were calculated for the charging process. The propagation of the melting and freezing front was also studied during the charging and discharging processes. The experimental results showed that in the charging process, the average heat transfer coefficient increases sharply with increasing the molten layer thickness, as the natural convection grows strong. In the discharge process, the useful heat gain was found to increase as the water mass flow rate increases (Fig. 7) [28].

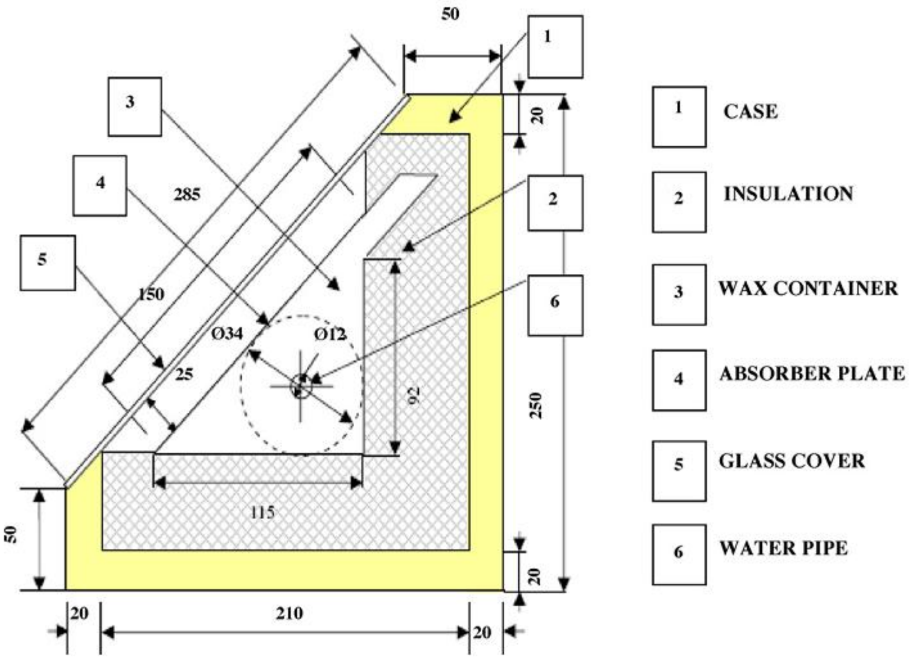

Figure 7: Schematic of the experimental apparatus cross-section [28].

Suat et al. [29] presented a conventional open-loop passive solar water-heating system combined with sodium thiosulfate pentahydrate-phase change material (PCM) were experimen-tally 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 hexahy-drate and sodium sulfate decahydrate (Glauber's salt) were examined theoretically by using meteorological data and thermophysical 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. It was also found that the hydrated salts of the highest solar thermal energy storage performance in PCMs used in theoretical investigation were disodium hydrogen phosphate dodecahydrate and sodium sulfate decahydrate (Fig. 8).

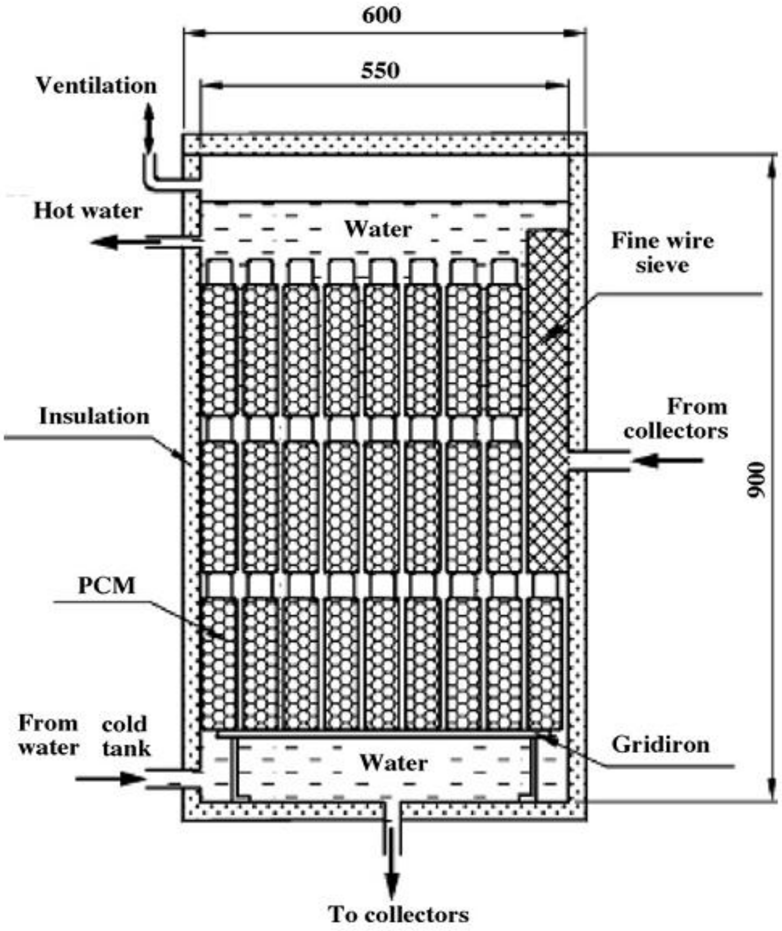

Figure 8 Detailed cross-sectional view of the cylindrical heat storage tank combined with PCM [29].

3.2.2 Solar air-heating systems

Morrison, Abdel Khalik and Jurinak in their different studies [30,31] evaluated the performance of air-based solar heating systems utilizing phase change energy storage unit. The main objectives of their work were:

(i) to determine the effect of the PCM latent heat and melting temperature on the thermal performance of air-based solar heating systems and
(ii) to develop empirical model of significant phase change energy storage (PCES) units.

The main conclusion was that the PCM should be selected on the basis of melting point rather than its latent heat and also found that air-based system utilizing sodium sulfate decahydrate as a storage medium requires roughly one-fourth the storage volume of a pebble bed and one-half the storage volume of a water tank.

Enibe [32] designed, development and performance evaluation of a natural convection solar air heater with phase change material energy storage has been successfully undertaken. The daytime performance of the system under no-load conditions was tested under natural environmental conditions involving ambient temperature variations in the range 19–41 °C and daily global irradiation in the range 4.9–19.9 MJ/m^2. Peak temperature rise of the heated air was about 15 K, while peak cumulative useful efficiency was about 50%. The 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 (Fig. 9).

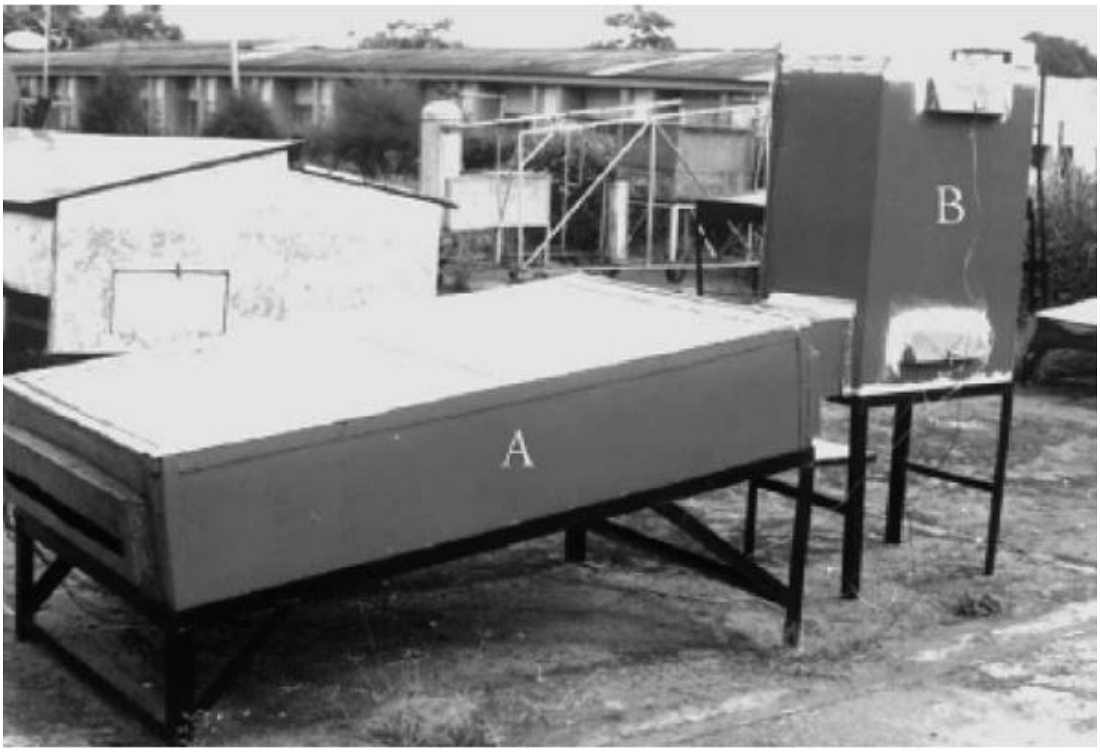

Figure 9: Photograph of the air heating system. (A) Collector assembly with energy storage and air-heating subsystems; (B) heated space[32].

3.2.3 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.

Domanski et al. [33] have studied the use of a PCM as a storage medium for a box type solar cooker designed to cook the food in the late evening hours and/or during the non-sunshine hours. They used magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) as a PCM for the heat storage.

Sharma et al. [34] developed a PCM storage unit with acetamide for a box type solar cooker to cook the food in the late evening (Fig.10). They recommended that the melting temperature of a PCM should be between 105 and 110 °C for evening cooking.

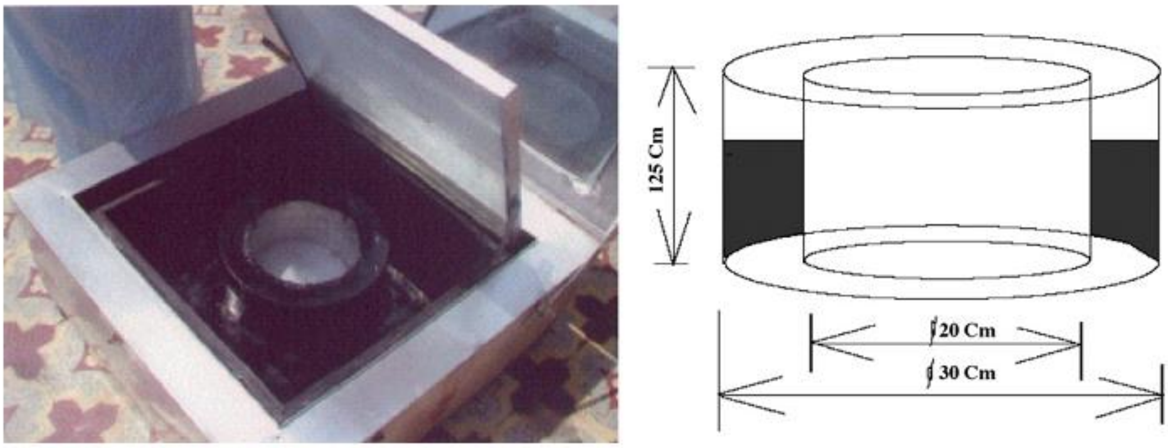

Figure 10 Schematic diagram of the box of a solar cooker with storage [34].

Sharma et al. [35] also used erythritol as a latent heat storage material for the solar cooker based on an evacuated tube solar collector (Fig. 11).

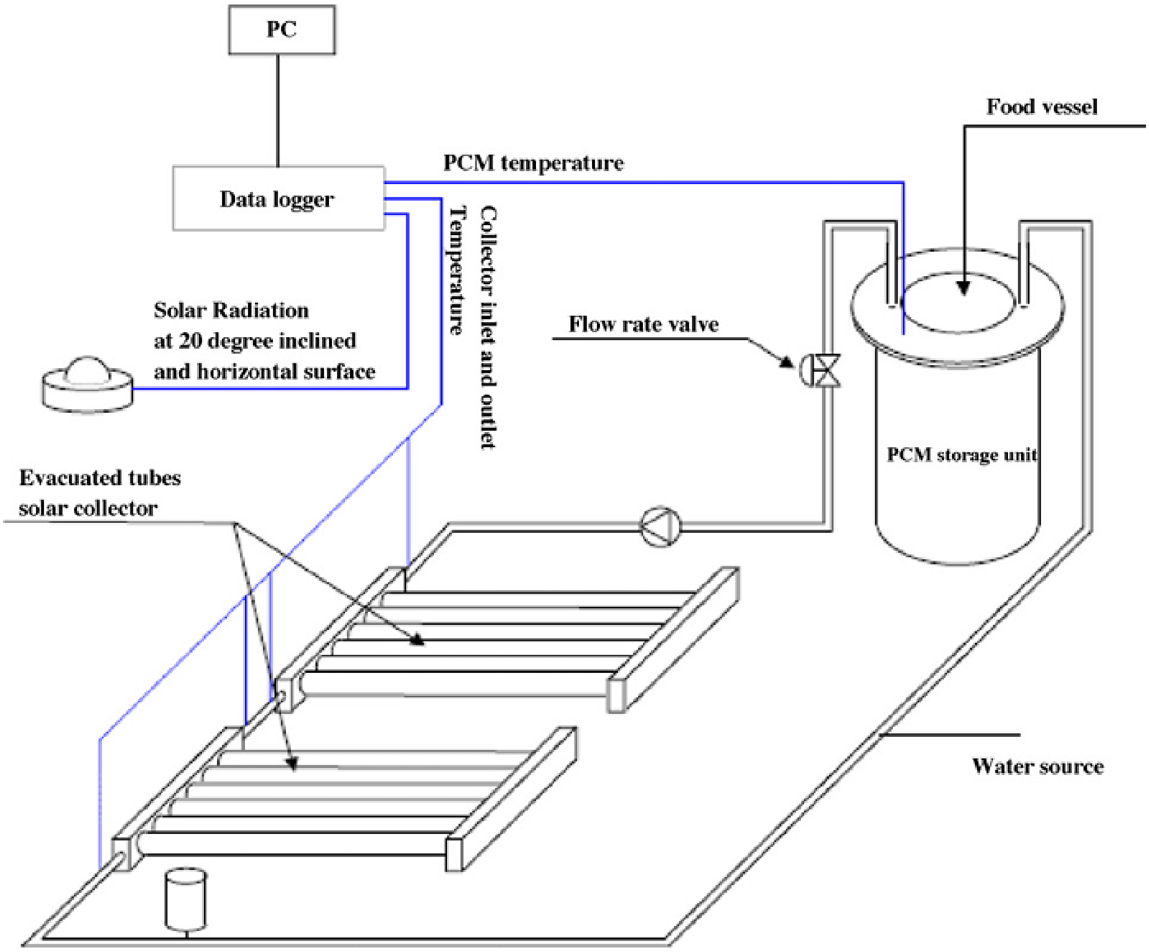

Figure 11 Outline of the prototype solar cooker based on evacuated tube solar collector with PCM storage unit [35].

3.2.4 Solar green house

Phase change materials have also been used in green houses for storing the solar energy for curing and drying process and plant production [36].

Kern and Aldrich [37] employed 1650 kg of $CaC_{12} \cdot 6H_2O$ in aerosol cans each weighing 0.74 kg was used to investigate energy storage possibilities both inside and outside a 36 m^2-ground area greenhouse covered with tedlarcoated fibreglass. PCM cans were placed in a store with 22.86 mm spacing and two stores containing different amounts of PCM was used, one inside and the other outside the greenhouse. While the energy storage unit inside the green-house collected warm air from the ridge of the greenhouse during the daytime, the direction of air flow was reversed for the energy releasing process at night (Fig. 12).

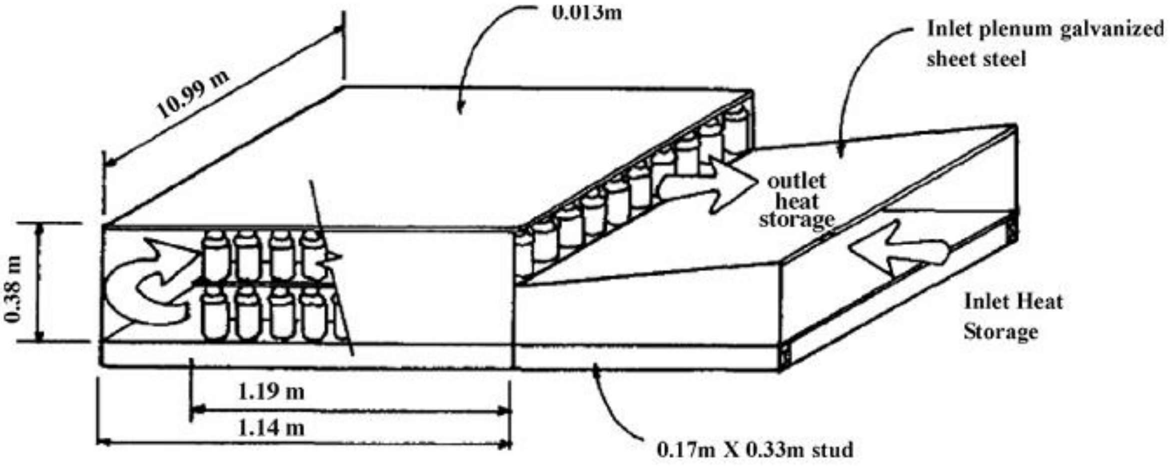

Figure 12: Energy storage unit inside the greenhouse [37].

Hung and Toksoy [38] 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 also revealed that the ring-baffled storage unit performed better than the cross-baffled storage unit. Using phase change material, experiments were conducted in a 500 m^2 single glazed greenhouse for the production of rose in France (Fig. 13). 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 solar greenhouse compartment with PCM storage was compared with a traditional greenhouse of identical geometry having the same plantation. The PCM green house achieved 80% savings in propane gas as compared with the traditional green house to have the same temperature. Latent heat storage material can also be stacked in racks placed in a greenhouse which will be directly heated by the solar radiation [38]. In this system the hot air was circulated in the greenhouse through the storage increase the rate of charging/discharging of PCM. The stored heat was utilized during off sunshine hours to maintain the desired temperature of the green house. $Na_2SO_4 \cdot 10H_2O$ was used as PCM storage material in the green house.

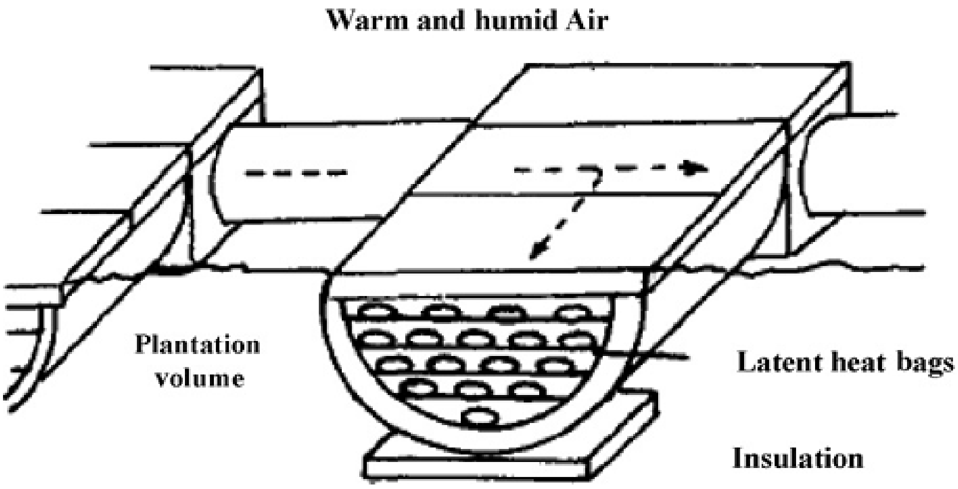

Figure 13: Underground tunnel with PCM Storage [38].

Ozturk [39] presented a seasonal thermal energy storage using paraffin wax as a PCM with the latent heat storage technique was attempted to heat the greenhouse of 180 m^2 floor area. The schematic arrangement of the LHS system for greenhouse heating is given in Fig. 14. The system consists mainly of five units: (1) flat plate solar air collectors (as heat collection unit), (2) latent heat storage (LHS) unit, (3) experimental greenhouse, (4) heat transfer unit and (5) data acquisition unit. The external heat collection unit consisted of 27 m^2 of south facing solar air heaters mounted at a 558 tilt angle. The diameter and the total volume of the steel tank used as the latent heat storage unit were 1.7 m and 11.6 m^3, respectively. The LHS unit was filled with 6000 kg of paraffin, equivalent to 33.33 kg of PCM per square meter of the greenhouse ground surface area. Energy and exergy analyses were applied in order to evaluate the system efficiency. The rate of heat transferred in the LHS unit ranged from 1.22 to 2.63 kW, whereas the rate of heat stored in the LHS unit was in the range of 0.65–2.1 kW. The average daily rate of thermal exergy transferred and stored in the LHS unit were 111.2 W and 79.9 W, respectively. During the experimental period, it was found that the average net energy and exergy efficiencies were 40.4% and 4.2%, respectively. The effect of the temperature difference of the heat transfer fluid at the inlet and outlet of the LHS unit on the computed values of the energy and exergy efficiency is evaluated during the charging period.

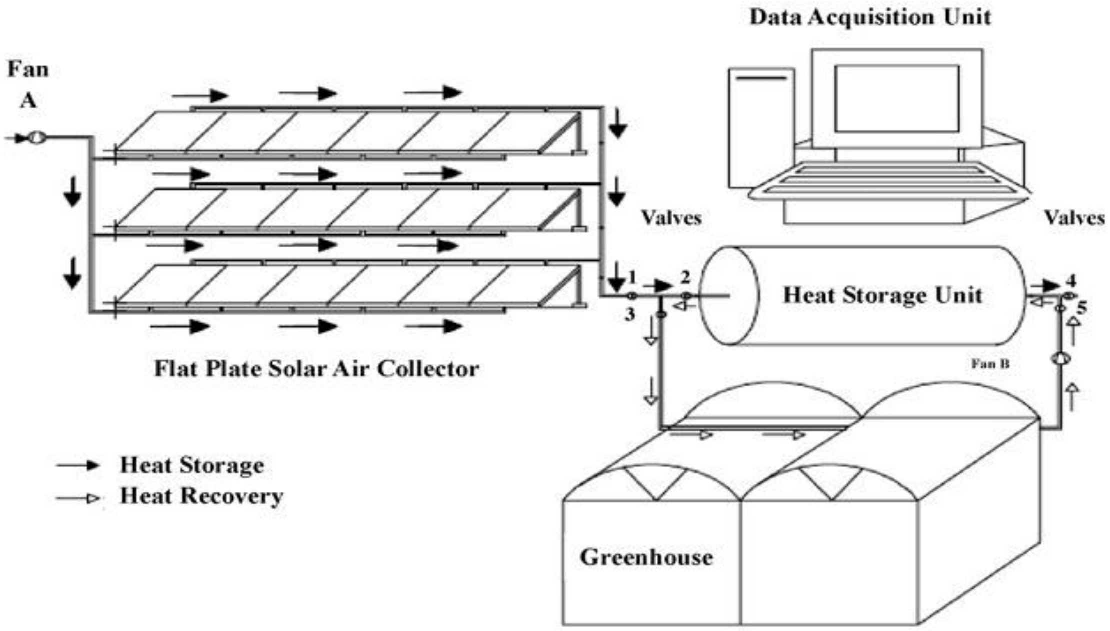

Figure 14: The arrangement of the heat storage and greenhouse heating system [39].

3.2.5 Buildings

PCMs have been considered for thermal storage in buildings since before 1980. With the advent of PCM implemented in Trombe wall, wallboards, shutters, under-floor heating systems and ceiling boards can be use as a part of the building for heating and cooling applications. In the literature, development and testing were conducted for prototypes of PCM wallboard and PCM concrete systems to enhance the thermal energy storage (TES) capacity of standard gypsum wallboard and concrete blocks, with particular interest in peak load shifting and solar energy utilization. The application of PCMs in building can have two different goals. First, using natural heat that is solar energy for heating or night cold for cooling. Second, using manmade heat or cold sources. In any case, storage of heat or cold is necessary to match availability and demand with respect to time and also with respect to power. Basically three different ways to use PCMs for heating and cooling of buildings are [40]:

(i) PCMs in building walls,

(ii) PCMs in other building components other than walls (windows, floor, ceiling boards), and

(iii) PCMs in heat and cold storage units.

3.2.6 Off-peak electricity storage

Telkes [41], Herrick [42] and Gawarn and Scroder [43] studied latent heat storage system for *air conditioning*. Inorganic hydrous salts were used as storage material. However these studies were focused more on the development of new heat storage materials. Lane[98] suggested some PCMs for *cooling and dehumidification*. The PCM is frozen during off-peak hours and coolness is withdrawn as needed during the day. Recently Department of Atomic Energy, Govt. of India sanctioned a R&D project to develop latent heat storage materials for the temperature range 5–15 °C for the storage of the coolness using off-peak power and to develop the pilot plant for the same [44] (Fig. 15). Several efforts have been made to develop PCM storage systems to utilize *off-peak electricity* [45-48]. Using off-peak electricity, phase change material can be melted/frozn to store electrical energy in the form of latent heat thermal energy and the heat/coolness then is available when needed. So, if latent heat thermal energy storage (LHTES) systems are coupled with the active systems, it will help in reducing the peak load and thus electricity generation cost can be reduced by keeping the demand nearly constant.

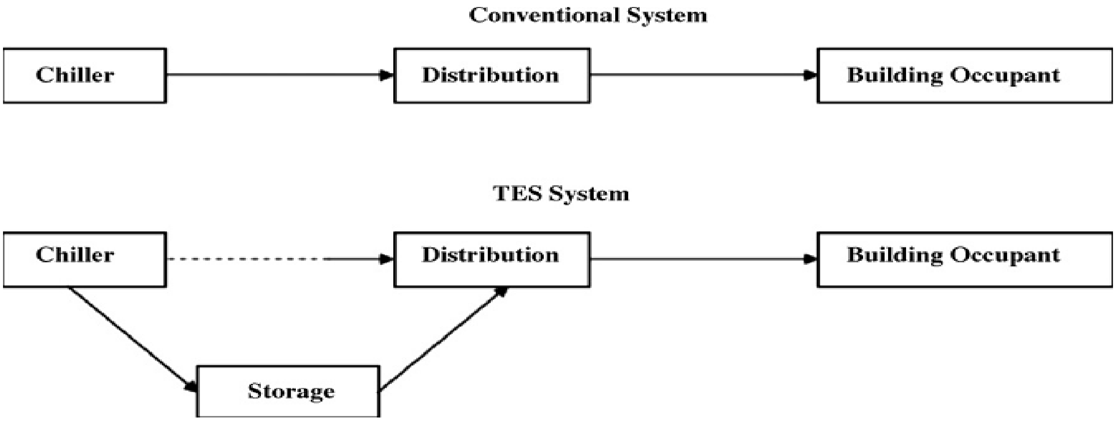

Figure 15: Major system cooling components [44].

Farid and Hussain [49] and Theunissen and Buchlin [50] developed an electrical storage heater utilizing off-peak electricity, usually available at night and the performance was tested experimentally and theoretically. Heat was stored in a commercial grade paraffin wax as latent heat of fusion to reduce the heavy weight of the existing storage heaters having sensible heat of storage. PCM was filled in multi units arranged to supply the necessary heat to the air flowing through them. Mostly active floor system can be used for off-peak storage of thermal energy in buildings. Thus, peak loads may be reduced and shifted to nighttime when electricity costs are lower. An electrical under-floor heating system having paraffin wax (melting point, 40 °C). They placed 30-mm layer of PCM between the heating surface and the floor tiles. Using computer simulation they found that the heat output of the floor could be raised significantly from 30 W/m^2 to 75 W/m^2 if PCM storage was used.

3.2.7 PCM technology for energy transportation

In order to utilize PCM technology for energy transportation using truck train or boat, the system needs to be designed for high volume fraction of PCM in order to maximize the energy density. Thus, either a system using direct contact between the PCM and heat transfer fluid (HTF), or a submerged heat exchanger concept would be the technically feasible options (as opposed to the more commonly suggested macro encapsulation of PCM in e.g. balls) [51].

The direct-contact technology has e.g. been proposed by the German company TransHeat. The TransHeat-Container (standard 20 feet or 40 feet freight container). Here, the company claimed a storage capacity per container can be 2.5 to 3.8 MWh depending on the PCM used [51].

Figure 16 shows the system.

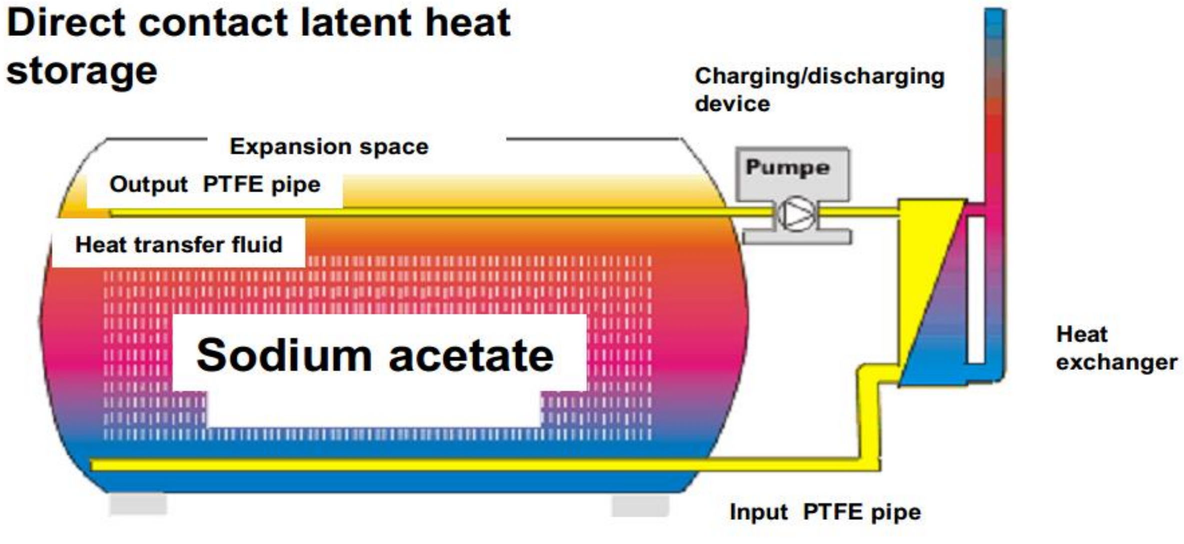

Figure 16: Direct contact mobile PCM container [51]

In the submerged heat exchanger concept, the heat transport in and out of the PCM is limiting the thermal power of the storage system. The German companies Alfred Schneider and LaTherm are using standard freight containers with an integrated heat exchanger (fig. 17) and Sodium acetate as PCM. This concept appears to be more stable and especially for mobile applications much more reliable. However, further development is needed for commercial realization of this concept.

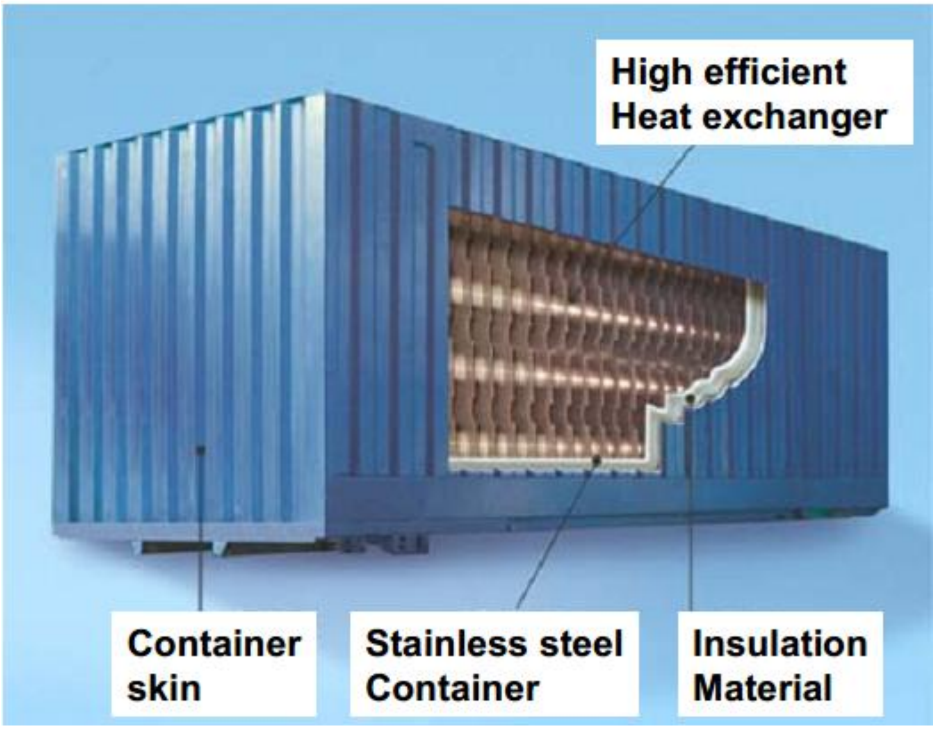

Figure 17: Container with integrated heat exchanger and PCM [52]

3.2.8 Industrial Waste Heat Utilization

The study refers to PCM storage with integrated heat exchanger and to the data from the company LaTherm (2-3 MWh thermal energy per container, 250 kW charging/discharging power and price per container 65000 €). A complete storage cycle will take 20 h plus the time for transportation and connecting the container to the charging/discharging station. That means one cycle per day could be possible.

The conclusion is transportation up to 30 km is economical interesting, even today. This is based on 350 cycles per year, which is almost a 100 % of the theoretical possible cycles per year. This assumption is very optimistic. The previously presented ZAE Bayern studies are based on a 60 % operation and the conclusion is that less than 10 km are the possible distance [53].

Fig. 18 shows the heat cost (€ ct./kWh) in dependence on the distance between source and consumer.

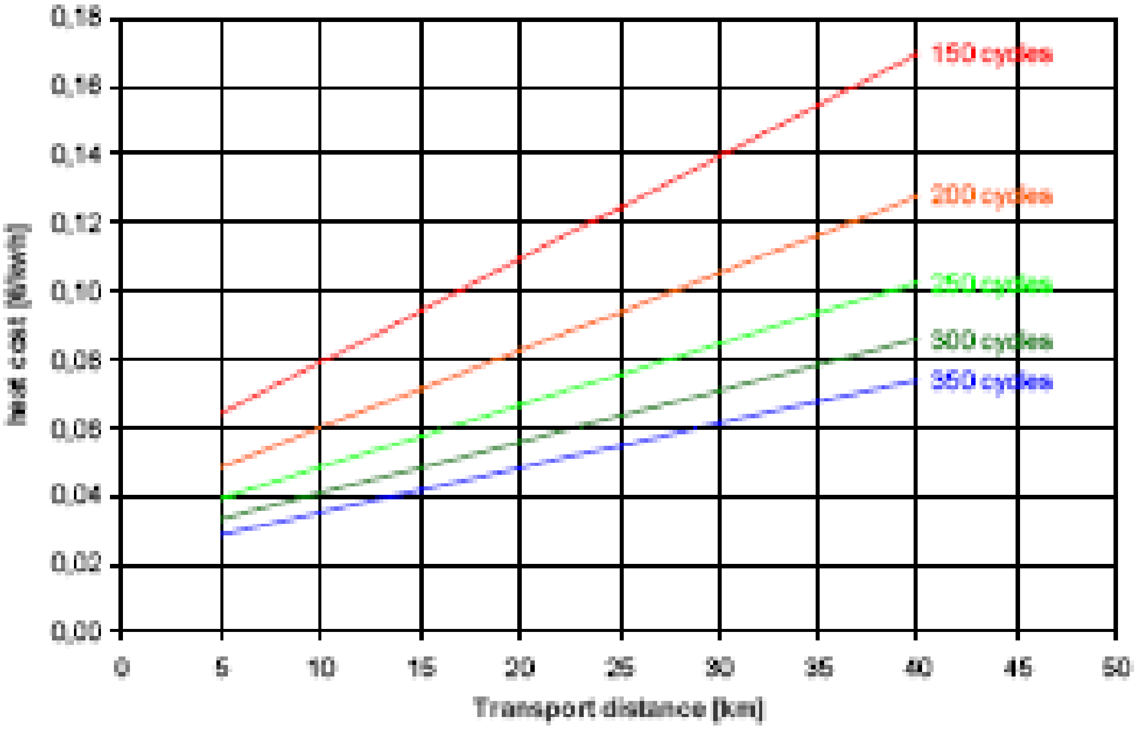

Figure 18: Heat cost depending on the distanc and the number of the charging/discharging cycles per year [53].

3.2.9 The transport of heat from a CHP plant to a local, small-scale district heating network.

In the city of Eskilstuna, Sweden, a biomassbased CHP plant (110 MW fuel) generates electricity and 330 GWh/year heat to the city's district heating network. The utility company also owns several small, local utilities with boilers only. One such network is the Ärla netwok with a 1 MW biomass boiler producing 5 GWh/year heat. The facility in Ärla also has a 200m^3 hot water accumulator capable of storing 8 MWh (between 40 and 80 °C) [53].

For the feasibility study, three candidate PCMs were evaluated assuming to be charged into a 40 feet standard container with a PCM volume fraction of 80%, allowing maximum weigh. Input data to the feasibility modelling is summarized in Table 4 [53].

Table 4: Fraction of transported energy vs PCM melting temperature, and desired supplay temperature [53]

Cost of Biomass Pellets, Ärla	30 €/MWh
Cost of Wood Chips, Central CHP Eskilstuna	20 €/MWh
Cost of Transportation	1.1 €/km
Cost of One Container	125000 €
Electricity Efficiency	30 %
Income of Electricity for Utility Company	50 €/MWh

In the study, a 40 tonnes MTES system, 40 ft container, is assumed since this is a feasible weight for Swedish Road Transportation. Also, and the power of such a container is taken as 1 MW which is reported possible for the directcontact PCM storage [51].

It needs to be pointed out, however, that ongoing experimental verification on this number is still to be presented in the literature. For a submerged heat exchanger concept, storage design is still needed which was previously described as one of the ongoing R&D activities of Ecostorage Sweden AB. Furthermore, two containers are assumed to be needed to always have surplus heat available at the demand side [53].

Table 5 summarizes the influence of the PCM properties on the amount of energy store per container.

Table 5: Melting temperature and storage capacity of the investigated PCMs [53]

	PCM Choice		
	Sodium Acetate, NaAc	$MgNO_3 \cdot 6H_2O$	Erythritol
Melting Temp. [°C]	58	89	120
Transported Heat (45-120 °C) per transport [MWh]	4.3	3.3	4.5
Latent Heat [kWh/tonne]	73	44	89

Figure 19 shows a summary of the results, considering the desired supply temperature to the heating network to be 80 °C [53].

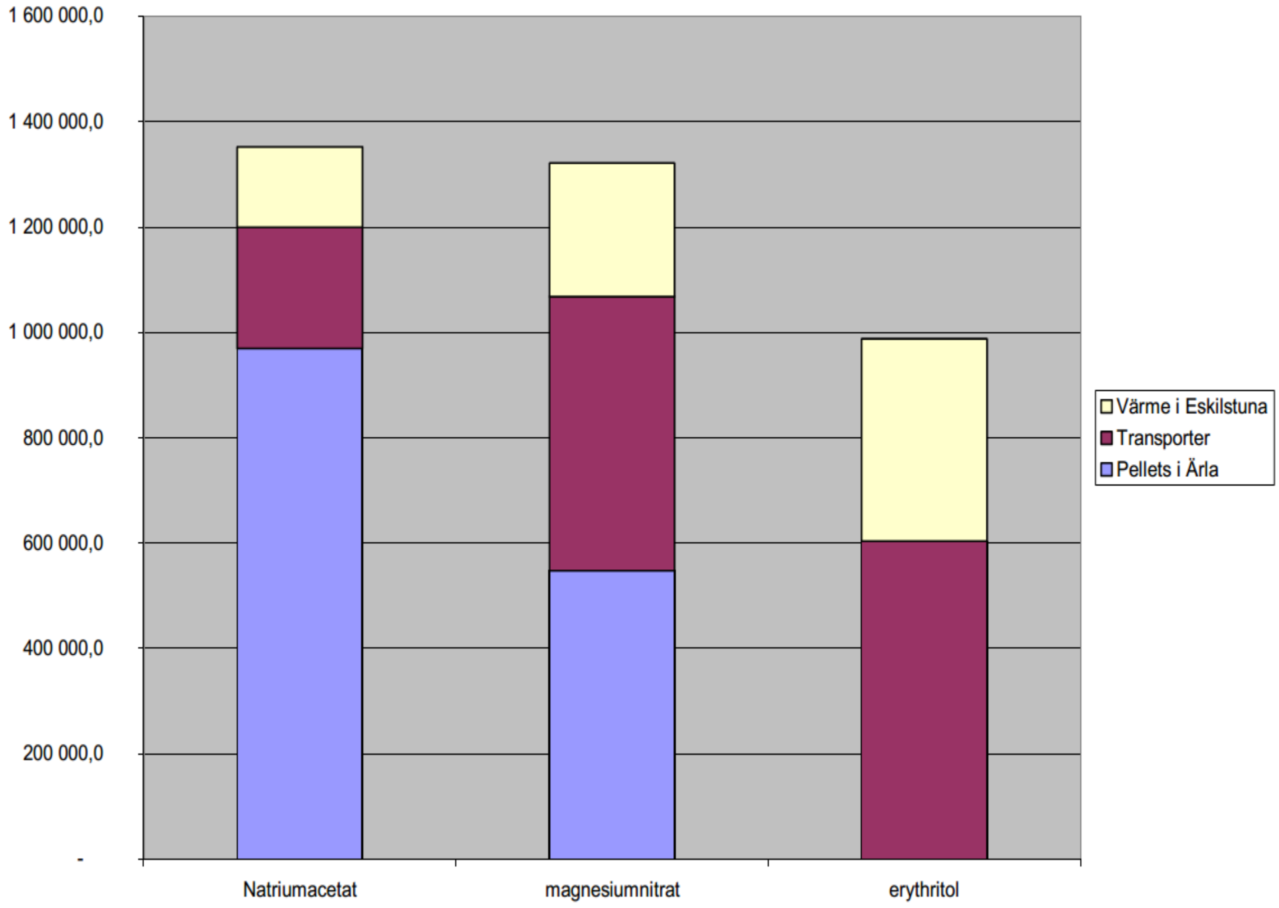

Figure 19: Anual cost for deliverd heat depending on the choice of PCM [53]

Here, it is shown that the total cost for transportation of heat is much higher when using a PCM with low melting temperature (NaAc) and low latent heat of phase change ($MgNO_3 \cdot 6H_2O$). A low melting temperature means that a large part of the transported heat is supplied at this low temperature such that a lot of auxiliary heat will be needed to ensure the desired supply temperature to the heating net. In the Erythritol case, no auxiliary heat is needed, and then the cost of transportation constitutes 60 % of the total cost. For a 40km transportation distance, the payback time is just below four years for the case of Erythritoland nine years for NaAc [53].

4 Physical properties of typically used PCM materials

All materials in nature, depending on the conditions, experience phase change; hence generally speaking, all materials can be considered as PCMs. However, only a relatively small group of them, for which the phase-change occurs in a technically interesting application, is indeed specifically called PCMs.

The most important physical properties of PCM materials from the thermal point of view are:

- phase-change temperature,
- latent heat, and
- thermal conductivity.

The most important difference between these materials is the phase change temperature. Each material makes its phase change at different temperature. In addition, each material has different value of latent heat and thermal conductivity. Energy densities for different *latent* and *sensible* heat storage materials are shown in table 4.

The main drawback of most of phase change materials is *their low thermal conductivity* that decreases the heat transfer rate. The most important feature for the selected phase change material is to have its *phase change temperature fitted to the application temperature range*.

Table 6: Energy densities for different *latent* and *sensible* heat storage materials [54]

a) Sensible heat storage

Material	**Formula**	**Specific heat (kJ/kg°C)**	**Volumetric heat capacity (kJ/m³°C)**
Water	H_2O	4,18	4191
Isobutyl alcohol	C_4H_9OH	3,01	2381
Ethyl alcohol	C_2H_5OH	2,85	2226
Beryllium	Be	2,81	5231
Limestone	$CaCO_3$	0,91	2548
Sand	SiO_2	0,80	1341
Iron	Fe	0,47	3688

b) Latent heat storage (solid to liquid)

Material	Formula	Melting point (°C)	Heat of fusion	
			(kJ/kg)	(kJ/m³)
Ethylene glycol	$C_2H_6O_3$	-13	146,50	162,800
Water	H_2O	0	334,90	305,500
Eastman 1-decanol	$C_{10}H_{22}O$	6	206,10	171,000
Sodium hydroxide 3½ hydrate	$2NaOH \cdot 7H_2O$	15	223,50	364,000
Glycerol	$C_3H_8O_3$	18	200,50	250,000
Sodium sulfate decahydrate	$Na_2SO_4 \cdot 10H_2O$	32	152,80	350,200
Calcium nitrate tetrahydrate	$Ca(NO_3)_2 \cdot 4H_2O$	42	152,80	288,700
Sodium hydroxide octahydrate	$NaOH \cdot 8H_2O$	64	272,10	472,000
Barium hydroxide octahydrate	$Ba(OH)_2 \cdot 8H_2O$	78	300,00	655,700
Sodium	Na	98	116,30	117,400
Benzoic acid	$C_2H_6O_2$	122	141,60	179,300
Ammonium thiocyanate	NH_4CNS	146	260,50	337,200
Lithium nitrate	$LiNO_3$	252	367,50	875,500
Sodium hydroxide	NaOH	300	225,60	465,700
Potassium perchlorate	$KClO_4$	527	1251,30	3148,000
Magnesium	Mg	651	239,10	499,000
Aluminum	Al	660	395,40	1655,000
Lithium hydried	LiH	685	3780,00	3100,000
Sodium chloride	NaCl	810	493,10	763,000
Sodium sulfate	Na_2SO_4	884	162,80	439,600
Magnesium fluroide	MgF_2	1266	930,30	2273,000
Iron	Fe	1533	151,20	1192,000

c) Latent heat storage (solid to solid transition)

Material	Formula	Transition temperature (°C)	Heat of transition (kJ/m³)
Vanadium tetraoxide	V_2O_4	72	208,600
Silver selenide	Ag_2Se	133	193,700
Ferrous sulfide	FeS	138	231,000

Following are the desirable properties of phase change materials used for latent thermal energy storage [55]:

1) Thermophysical Properties

a) *Suitable phase change temperature* T_{pc} → to assure storage and relase of heat in an application with given temperatures for heat source and heat sink.

b) *High latent heat of fusion per unit mass* Δh_{pc} → to achive high storage density compared to sensible heat storage.

c) *High thermal conductivity* in both liquid and solid phases →to be able to store or release the latent heat in a given volume of the storage material in a short time, that is with sufficient heating or cooling power.

d) *Low volume change* during the phase change → to reduce requirements of mechanical stability and tightness on a vessel containing the PCM.

e) *No subcooling during freezing* → to assure that melting and solidification can proceed in a narrow temperature range. Subcooling (also called supercooling) is the effect that a temperature significantly below the melting temperature has to be reached, until a material begins to solidify and relase heat (Fig. 19). If that temperature is not reached, the PCM will not solidify at all and thus only store sensible heat.

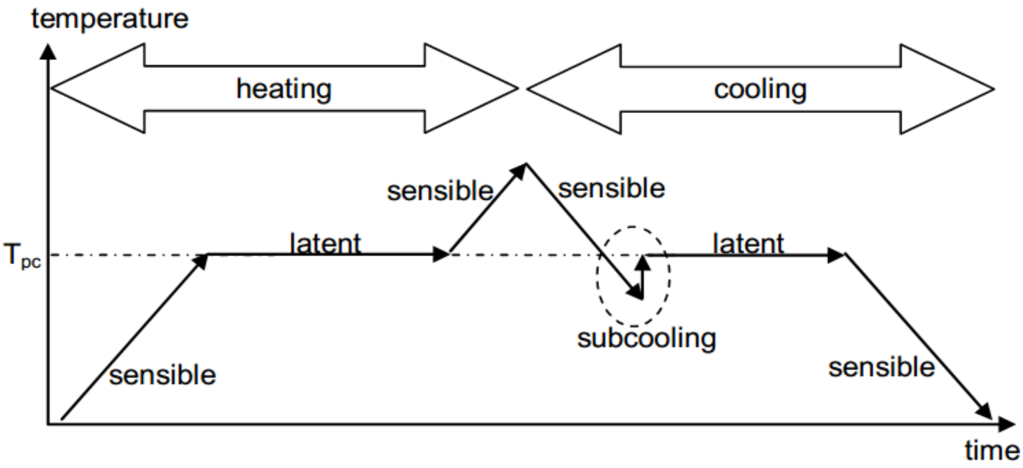

Figure 20: Schematic temperature change during heating (melting) and cooling (solidification) of a PCM with subcooling [15]

f) *Low vapor pressure* → to reduce requierments of mechanical stability and tightness on a vessel containing the PCM.

g) *Low density variation* during phase change

h) *High specific heat* to give additional benefits of sensible heat storage

2) Chemical Properties

a) *Chemical stability* after many cycles of operation → to assure long lifetime of the PCM if it is exposed to higher temperatures, radiation, gases, ...

b) *No phase separation* or *chemical decomposition*

c) *No degradation* after many cycles of operation → to use the storage material as many times for storage and release of heat as required by an application.

d) *Non flammable*, *non corrosive*, and *non toxic*

3) Availability and Cost

a) *Low price* → to be competitive with other options for heat and cold storage, and to be compatitive with methods of heat and cold supply without storage at all.

b) *Good recyclability* → for environmental and economic reasons.

Indeed, there is no specific material that can be regarded ideal phase change material; each material has its advantages and disadvantages. The choice of the PCM is the result of a trade-off among all its properties, depending on the target application.

4.1 Classification of Phase Change Materials

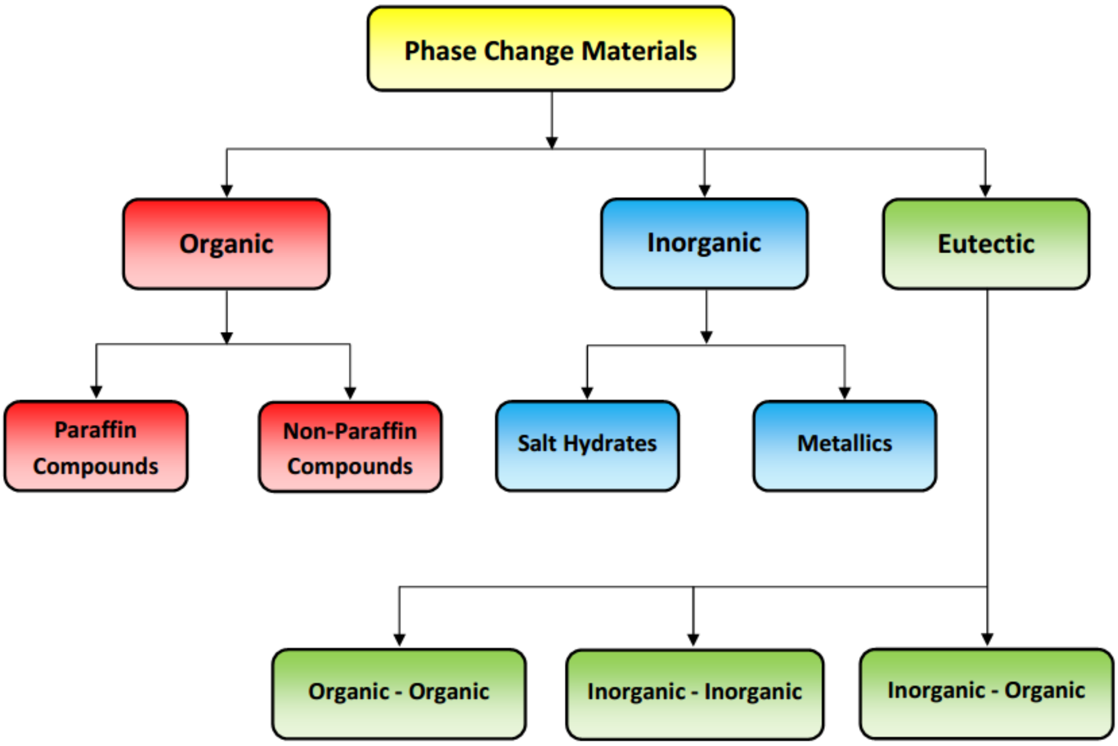

Figure 21: Classification of phase change materials [54]

A) Organic Phase Change Materials

Organic phase change materials are classified as *paraffins* and *non-paraffins*. Organic PCMs are characterized by their ability to melt and freeze many times without phase segregation and degradation of their latent heat of fusion [56].

1) **Paraffins**

Paraffins of type C_nH_{2n+2} are a group 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 one of the most popular organic heat storage PCM for commercial applications. It consists of a straight chain hydrocarbons having *melting temperatures between* 23°C *and* 67°C [57]. Following are some of the advantages and disadvantages of paraffins [56] [57]:

Advantages:

- paraffins are available in a *large temperature range*,
- paraffins have no tendencies to super cool,
- paraffins are chemically stable,
- paraffin waxes show *high heats of fusion*,
- paraffin waxes don’t segregate,
- paraffin waxes are safe,
- paraffins are non-corrosive.

Disadvantages:

- Low thermal conductivity,
- high volume change between the solid and liquid phases,
- commercial paraffins *do not have sharp exact melting points*,
- paraffins are *flammable*,
- pure paraffins are *expensive*,
- technical grade paraffins (which has properties worse than pure paraffins) is commonly used as PCMs for thermal energy storage because it is cheaper than pure paraffins,

Thermo physical properties (melting temperature, density, thermal conductivity, and latent heat of fusion) for some selected paraffins are shown in table 5.

Table 7: Thermophysical properties for some paraffin PCMs [57]

Name	No. of "C" Atoms	Melting point (°C)	Density (kg/m³)	Thermal Conductivity (W/mK)	Latent heat of fusion (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	0,35^S[14]; 0,149^L[14]	245
n - Nonadecane	19	31,9	912^S; 769^L	0,21^S	222
n - Eicosanc	20	37			247
n - Heneicoscane	21	41			215
n - Docosane	22	44			249
n - Tricosane	23	47			234
n - Tetracoscane	24	51			255
n - Pentacosane	25	54			238
Paraffin - Wax	n.a.	32	785^S[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

2) Non-Paraffins

The non-paraffin organic are the most numerous of the phase change materials with highly varied properties. Non-paraffin organic PCMs are characterized by their varied properties. Each of these materials will have its own properties unlike the paraffin's, which have very similar properties. Abhat et al. [58], Buddhi and Sawhney [59] have conducted an extensive survey and recognized a number of esters, fatty acids, alcohols, and glycols suitable for thermal energy storage. These organic materials are subdivided into fatty acids and other non-paraffin organic [56]. These materials are flammable and should not be exposed to excessively high temperature, flames or oxidizing agents. Following are some advantages and disadvantages of non paraffins [56]:

Advantages

- High heat of fusion

Disadvantages

- Low thermal conductivity,
- low flash points,
- inflammability,
- instability at high temperatures,
- varying level of toxicity.

Table 6 shows the melting temperature and latent heat of fusion for some non-paraffin materials that can be used as phase change materials.

Table 8: Melting temperature and latent heat of fusion of some non-paraffin PCMs [56]

Material	Melting point (°C)	Latent heat (kJ/kg)	*Group
Formic acid	7,8	247	III
Caprilic acid	16,3	149	/
Glycerin	17,9	198,7	III
D-Lattic acid	26	184	I
Methyl palmitate	29	205	II
Camphenilone	39	205	II
Docasyl bromide	40	201	II
Caprylone	40	259	II
Phenol	41	120	III
Heptadecanone	41	201	II
1-Cyclohexylocctadecane	41	218	II
4-Heptadacanone	41	197	II
p-Joluidine	43,3	167	/
Cyanamide	44	209	II
Methyl eicosanate	45	230	II
3-Heptadecanone	48	218	II
2-Heptadecanone	48	218	II
Hydrocinnamic acid	48	118	/
Cetyl alcohol	49,3	141	/
α-Nepthylamine	50	93	/
Camphene	50	238	III
O-Nitroaniline	50	93	/
9-Heptadecanone	51	213	II

Thymol	51,5	115	/
Methyl behenate	52	234	II
Diphenyl amine	52,9	107	/
p-Dichlorobenzene	53,1	121	/
Oxolate	54,3	178	/
Hypophosphoric acid	55	213	II
O-Xylene dichloride	55	121	/
β-Chloroacetice acid	56	147	III
Chloroacetic acid	56	130	III
Nitro naphthalene	56,7	103	/
Trimyristin	33-57	201-213	I
Heptaudecanoic acid	60,6	189	II
α-Chloroacetic acid	61,2	130	/
Bee wax	61,8	177	II
Bees wax	61,8	177	II
Glyolic acid	63	109	/
Glycolic acid	63	109	/
p-Bromophenol	63,5	86	/
Azobenzen	67,1	121	/
Acrylic acid	68	115	/
Dinto toluent (2,4)	70	111	/
Phenylacetic acid	76,7	102	/
Thiosinamine	77	140	/
Bromcamphor	77	174	/
Durene	79,3	156	/
Benzylamine	78	174	/
Methyl brombrenzoate	81	126	/
Alpha napthol	96	163	/
Glautaric acid	97,5	156	/
p-Xylene dichloride	100	138,7	/
Catechol	104,3	207	III
Quinone	115	171	II
Acetanilide	118,9	222	II
Succinic anhydride	119	204	II
Benzoic acid	12,7	142,8	III
Stibene	124	167	/
Benzamide	127,2	169,4	III

***Group I, most promising; group II, promising; group III, less promising; / insufficient data**

- **Fatty acids**

General formula for all the fatty acid is given by CH_3 $(CH2)_{2n}$ × COOH. Fatty acids have the same characteristics as paraffins [57] and have high values of latent heat of fusion compared to paraffins. Fatty acids have the ability of many cycling of melting and freezing with no supercooling, and they are characterized by sharperphase temperature than technical grade paraffins. The major drawback of fatty acids is their high cost that is 2–2.5 times greater than that of the technical grade paraffins. Additionally, they are mild corrosive [56].

Melting temperature and latent heat of fusion for some fatty acids for low temperature latent thermal energy storage applications are shown in table 7.

Table 9: Melting temperature and latent heat of fusion of some fatty acid PCMs [56]

Material	**Formula**	**Melting point (°C)**	**Latent heat (kJ/kg)**	***Group**
Acetic acid	CH_3COOH	16,7	184	I
Polyethylene glycol 600	$H(OC_2H_2)_n{\cdot}OH$	20-25	146	I
Capric acid	$CH_3(CH_2)_8{\cdot}COOH$	36	152	/
Eladic acid	$C_8H_7C_9H_{16}{\cdot}COOH$	47	218	I
Lauric acid	$CH_3(CH_2)_{10}{\cdot}COOH$	49	178	II
Pentadecanoic acid	$CH_3(CH_2)_{13}{\cdot}COOH$	52,5	178	/
Tristearin	$(C_{17}H_{35}COO)C_3H_5$	56	191	I
Myristic acid	$CH_3(CH_2)_{12}{\cdot}COOH$	58	199	I
Palmatic acid	$CH_3(CH_2)_{14}{\cdot}COOH$	55	163	I
Stearic acid	$CH_3(CH_2)_{16}{\cdot}COOH$	69,4	199	I
Acetamide	CH_3CONH_2	81	241	I
Methyl fumarate	$(CHCO_2NH_3)_2$	102	242	I

***Group I, most promising; group II, promising; group III, less promising; / insufficient data**

B) Inorganic Phase Change Materials

Inorganic phase change materials are classified as salt hydrates and metallics. These phase change materials do not supercool appreciably and their heats of fusion do not degrade with cycling.

1) Salt hydrates

Salt hydrates consist of a salt and water that combine in a crystalline matrix when the material solidifies. There are many different salt hydrates having melting temperature ranges between 15°C - 117°C. Salt hydrates are considered as the most important group of PCMs that have been studied for application in latent thermal energy storage systems [57]. Glauber salt ($Na_2SO_4.10H_2O$) consists of 44% Na_2SO_4 and 56% H_2O by weight. It has a melting temperature around 32.4°C, a latent heat of fusion of 254 kJ/kg (377 MJ/m^3), and is one of the cheapest materials that can be used for latent thermal energy storage; Its main drawback is the problems of phase segregation and subcooling [59].

Following are the advantages and disadvantages of salt hydrates [56] [57]:

Advantages

- High latent heat of fusion per unit mass and volume(higher than paraffins),
- high thermal conductivity (compared with paraffins),
- have sharp phase change temperature,
- small volume changes during melting,
- high availability,
- low cost.

Disadvantages

- Segregation: segregation is the formation of other hydrates or dehydrated salts that settle and reduce the volume that is available for thermalenergy storage [57],
- Salt hydrates show super cooling because they are unable to start crystallization at the freezing temperature. This problem can be avoided by using nucleating agents [57],
- Salt hydrates cause corrosion in metal containers, whereas metal containers are the common containers used in thermal energy storage systems [57]

Table 8 shows the melting temperature and latent heat of fusion for some salt hydrates suitable for low temperature thermal energy storage, while table 8 shows the melting temperature and latent heat of fusion for some other salt compounds that are suitable for high temperature thermal energy storage.

Table 10: Melting temperature and latent heat of fusion for salt hydrates used as PCMs for low temperature thermal energy storage [56]

Material	**Melting point (°C)**	**Latent heat (kJ/kg)**	***Group**
$K_2HPO_4 \cdot 6H_2O$	14	109	II
$FeBr_3 \cdot 6H_2O$	21	105	II
$Mn(NO_3)_2 \cdot 6H_2O$	25,5	148	II
$FeBr_3 \cdot 6H_2O$	27	105	II
$CaCl_2 \cdot 12H_2O$	29,8	174	I
$LiNO_3 \cdot 2H_2O$	30	296	I
$LiNO_3 \cdot 3H_2O$	30	189	I
$Na_2CO_3 \cdot 10H_2O$	32	267	II
$Na_2SO_4 \cdot 10H_2O$	32,4	241	II
$KFe(SO_4)_2 \cdot 12H_2O$	33	173	I
$CaBr_2 \cdot 6H_2O$	34	138	II
$LiBr_2 \cdot 2H_2O$	34	124	I
$Zn(NO_3)_2 \cdot 6H_2O$	36,1	134	III
$FeCl_3 \cdot 6H_2O$	37	223	I
$Mn(NO_3)_2 \cdot 4H_2O$	37,1	115	II
$Na_2HPO_4 \cdot 12H_2O$	40	279	II
$CoSO_4 \cdot 7H_2O$	40,7	170	I
$KF \cdot 2H_2O$	42	162	III
$MgI_2 \cdot 8H_2O$	42	133	III
$CaI_2 \cdot 6H_2O$	42	162	III
$K_2HPO_4 \cdot 7H_2O$	45	145	II
$Zn(NO_3)_2 \cdot 4H_2O$	45	110	III
$Mg(NO_3)_2 \cdot 4H_2O$	47	142	II
$Ca(NO_3)_2 \cdot 4H_2O$	47	153	I
$Fe(NO_3)_2 \cdot 9H_2O$	47	155	I
$Na_2SiO_3 \cdot 4H_2O$	48	168	II
$K_2HPO_4 \cdot 3H_2O$	48	99	II
$Na_2S_2O_3 \cdot 5H_2O$	48,5	210	II
$MgSO_4 \cdot 7H_2O$	48,5	202	II
$Ca(NO_3)_2 \cdot 3H_2O$	51	104	I
$Zn(NO_3)_2 \cdot 2H_2O$	55	68	III
$FeCl_3 \cdot 2H_2O$	56	90	I
$Ni(NO_3)_2 \cdot 6H_2O$	57	169	II
$MnCl_2 \cdot 4H_2O$	58	151	II
$MgCl_2 \cdot 4H_2O$	58	178	II
$CH_3COONa \cdot 3H_2O$	58	265	II
$Fe(NO_3)_2 \cdot 6H_2O$	60,5	126	/
$NaAl(SO_4)_2 \cdot 10H_2O$	61	181	I
$NaOH \cdot 2H_2O$	64,3	273	I

$Na_3PO_4 \cdot 12H_2O$	65	190	/
$LiCH_3COO \cdot 2H_2O$	70	150	II
$Al(NO_3)_2 \cdot 9H_2O$	72	155	I
$Ba(OH)_2 \cdot 8H_2O$	78	265	II
$Mg(NO_3)_2 \cdot 6H_2O$	89,9	167	II
$KAl(SO_4)_2 \cdot 12H_2O$	91	184	II
$MgCl_2 \cdot 6H_2O$	117	167	I

***Group I, most promising; group II, promising; group III, less promising; / insufficient data**

Table 11: Melting temperature and latent heat of fusion for some salt compounds used as PCMs for high temperature thermal energy storage [60]

Metal	Fluioride	Chloride	Bromide	Iodide	Sulphate	Nitrate	Carbonate	Chromate	Molybdate	Tungstate
Melting temperature, °C										
Lithium	849	610	550	469	858	253	732	485	703	740
Sodium	996	801	742	661	884	307	858	794	688	696
Potassium	858	771	734	681	1069	335	900	973	926	923
Rubidium	795	723	692	556	1070	312	873	994	955	952
Cesium	703	645	638	632	1015	409	793	975	935	953
Magnesium	1263	714	711	633	1137	426	990		1230	826
Calcium	1418	772	742	783	1460	560	1330	1000	1449	1580
Strontium	1477	875	657	538	1605	645	1490	1283	1457	1535
Barium	1368	961	857	711	1680	594	1555	1444	1458	1475
Heat of fusion, J/g										
Lithium	1041	416	203		84	373	509	168	281	157
Sodium	794	482	255	158	165	177	165	146	109	107
Potassium	507	353	215	145	212	88	202	41	163	86
Rubidium	248	197	141	104	145	31			140	78
Cesium	143	121	111	96	101	71		94	75	63
Magnesium	938	454	214	93	122		698			
Calcium	381	253	245	142	203	145				
Strontium	226	103	41	57	196	231				
Barium	105	76	108	68	175	209				

2) Metallics

Metallics include the low melting metals and metal eutectics. Metallics have not been strongly studied as PCM for latent heat storage because of their heavy weights. For the applications that weight is not an important issue while volume is animportant parameter, metallics are attractive because of their high heat of fusion perunit volume [56].

Some features of these materials are: [56]

- low heat of fusion per unit weight,
- high heat of fusion per unit volume,
- high thermal conductivity,
- low specific heat,
- relatively low vapour pressure

Table 10 gives the melting temperature and latent heat of fusion for some metallics that can be used as phase change materials for latent thermal energy storage.

Table 12: Melting temperature and latent heat of fusion for some metallic PCMs [56]

Material	**Melting point (°C)**	**Latent heat (kJ/kg)**	***Group**
Gallium-gallium antymony eutectic	29,8		/
Gallium	30	80,3	I
Cerrolow eutectic	58	90,9	/
Bi-Cd-In eutectic	61	25	/
Cerrobend eutectic	70	32,6	I
Bi-Pb-In eutectic	70	29	/
Bi-In eutectic	72	25	/
Bi-Pb -tin eutectic	96		/
Bi-Pb eutectic	125		/

***Group I, most promising; group II, promising; group III, less promising; / insufficient data**

3) Eutectics

The eutectics consist of two or more components where each of them melts and freezes congruently forming a mixture of a component that crystals during crystallization process [61] [56]. Usually, eutectics melt and freeze without segregation. During melting process, both components liquefy at the same time without possibility of separation [56]. A list of some eutectic compounds is given in table 11.

Table 13: List of organic and inorganic eutectics PCMs [56]

Material	Composition (wt.%)	Melting point (°C)	Latent heat (kJ/kg)	*Group
$CaCl_2 \cdot 6H_2O + CaBr_2 \cdot 6H_2O$	45+55	14,7	140	/
Triethylolethane+water+urea	38,5+31,5+30	13,4	160	I
$C_{14}H_{28}O_2 + C_{10}H_{20}O_2$	34+66	24	147,7	/
$CaCl_2 + MgCl_2 \cdot 6H_2O$	50+50	25	95	II
$CH_3CONH_2 + NH_2CONH_2$	50+50	27	163	II
Triethylolethane+urea	62,5+37,5	29,8	218	I
$Ca(NO_3) \cdot 4H_2O + Mg(NO_3)_3 \cdot 6H_2O$	47+53	30	136	/
$CH_3COONa \cdot 3H_2O + NH_2CONH_2$	40+60	30	200,5	I
$NH_2CONH_2 + NH_4NO_3$	53+47	46	95	II
$Mg(NO_3)_3 \cdot 6H_2O + NH_4NO_3$	61,5+38,5	52	125,5	I
$Mg(NO_3)_3 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$	58,7+41,3	59	132,2	I
$Mg(NO_3)_3 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$	50+50	59,1	144	/
$Mg(NO_3)_3 \cdot 6H_2O + Al(NO_3)_2 \cdot 9H_2O$	53+47	61	148	/
$CH_3CONH_2 + C_{17}H_{35}COOH$	50+50	65	218	/
$Mg(NO_3)_2 \cdot 6H_2O + MgBr_2 \cdot 6H_2O$	59+41	66	168	I
Nepthalene+benzoic acid	67,1+32,9	67	123,4	/
$NH_2CONH_2 + NH_4Br$	66,6+33,4	76	151	II
$LiNO_3 + NH_4NO_3 + NaNO_3$	25+65+10	80,5	113	/
$LiNO_3 + NH_4NO_3 + KNO_3$	26,4+58,7+14,9	81,5	116	/
$LiNO_3 + NH_4NO_3 + NH_4Cl$	27+68+5	81,6	108	/

***Group I, most promising; group II, promising; group III, less promising; / insufficient data**

4.2 Commercial Phase Change Materials

Most commercial PCM are based on materials from the material classes of the salt hydrates, paraffins, and eutectic water-salt solutions. They are however not identical with these materials. In the case of salt hydrates, often the composition is changed, a nucleator is added, the material is gelled or thickened, or the PCM is a mixture of different base materials. With paraffins, commercial grade paraffins usually contain a mixture of different alcanes because pure alcanes are expensive. Commercial PCM cover the temperature range from – 40 °C to +120 °C. Even though many materials have been investigated for higher temperatures, none of them is available commercially because there has been no market yet [62].

4.2.1 PCM composite materials

A composite material is a material that iscomposed of several different materials, usually to improve a property of a material or to combine properties of different materials. In the case of PCM, a PCM composite material is produced to improve at least one of the PCM properties or to improve the heat storage capacity of another material. There are different ways to form a composite: by embedding PCM in a matrix of another material, or by embedding another material into the PCM [63].

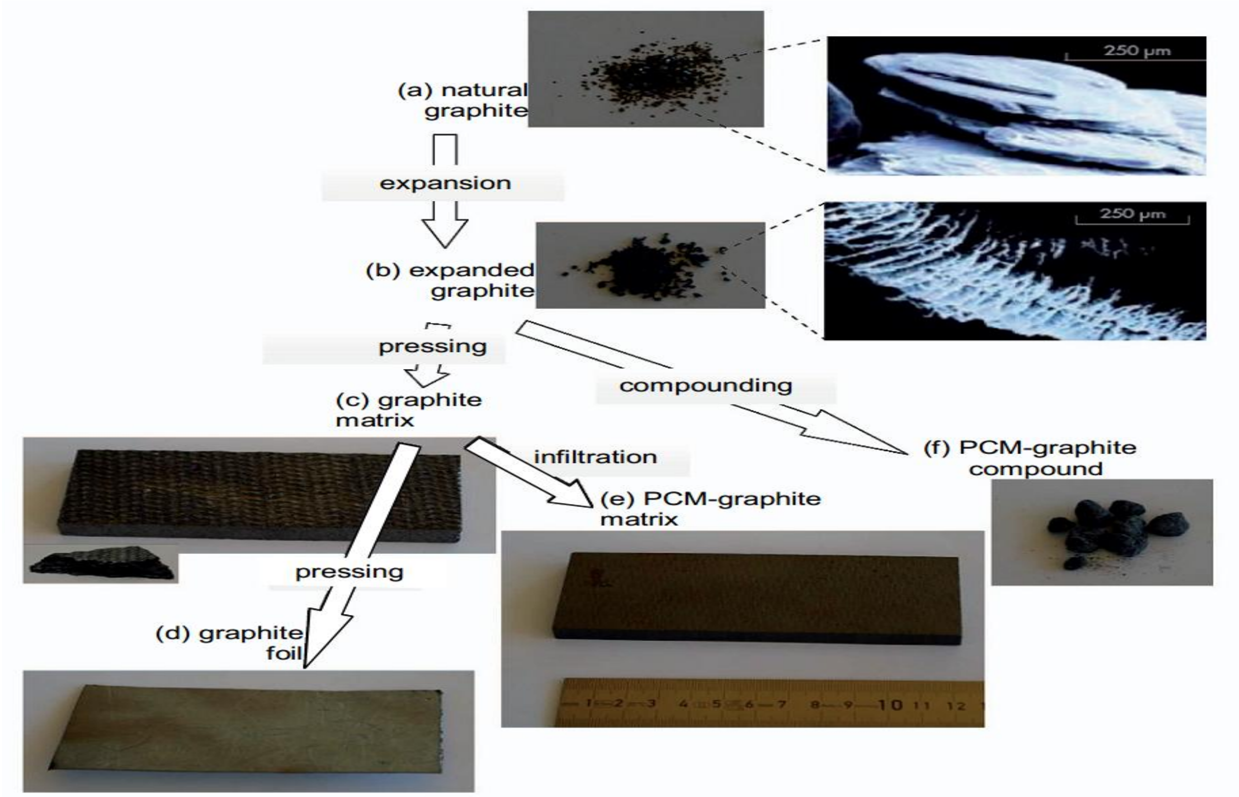

Figure 22: Processing of graphite from natural graphite to different products. All pictures have the same scale (microscopic images of expanded graphite: SGL TECHNOLOGIES GmbH)[63].

Fig.21. shows the processing from natural graphite to different products. The first processing step starts with natural graphite (a) with a density of about 2200 kg/m^3. After a chemical treatment, the following thermal treatment of the natural graphite starts a chemical reaction, which produces gases. These gases lead to an expansion of the graphite structure as the microscopic image in fig.21. shows. The particles of the expanded graphite (b) have a highly porous structure and dimensions in the order of one to several mm. This gives them a bulk density of about 3 kg/m^3, less than 0.2% of the density of natural graphite. In other words, 99.8% of the volume is pores [63].

4.2.2 Encapsulated PCM

Encapsulations are classified according to their size as macro and micro-encapsulation. Macroencapsulation is by far the most widely used type of encapsulation, see Fig. 22, however also microencapsulated PCM are produced on an industrial scale nowadays. When encapsulating PCM, it is necessary to take into account several aspects. First, the material of the container wall must be compatible with the PCM. Then, taking into account the selected wall material, the container wall has to be sufficiently thick to assure the necessary diffusion tightness Finally, the encapsulation must be designed in a way that it is able to cope with the mechanical stress on the container walls caused by the volume change of the PCM.

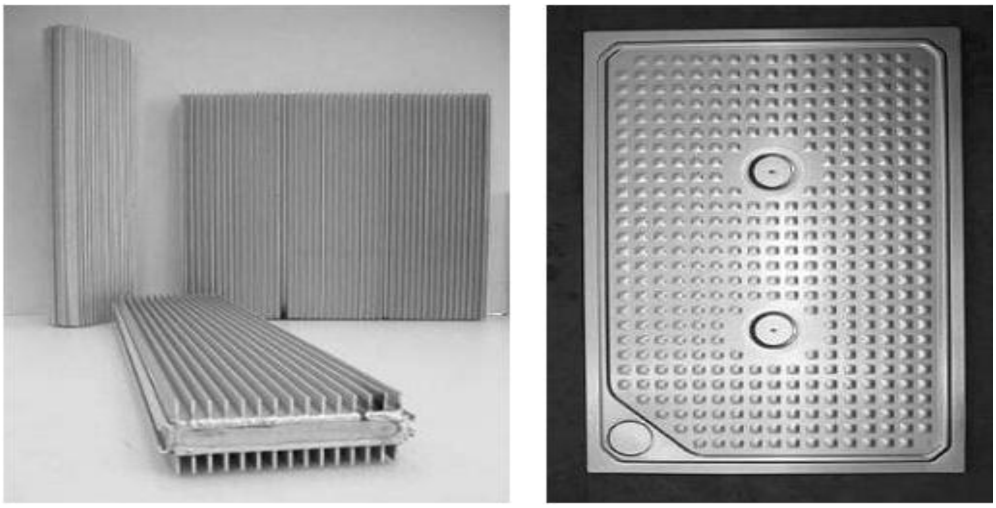

Figure 23: Macroencapsulation in metal containers: left, aluminum profiles with fins for improved heat transfer from Climator (picture: Climator), and right, coated aluminum plate from Rubitherm Technologies GmbH (picture: Rubitherm Technologies GmbH) [63].

Microencapsulation of PCM is technically feasible today only for organic materials. Commercial products seem to use exclusively paraffins. Fig.23. shows commercial microencapsulated paraf-fin, with a typical capsulediameter in the 2-20 µm range, produced by the com-pany BASF.

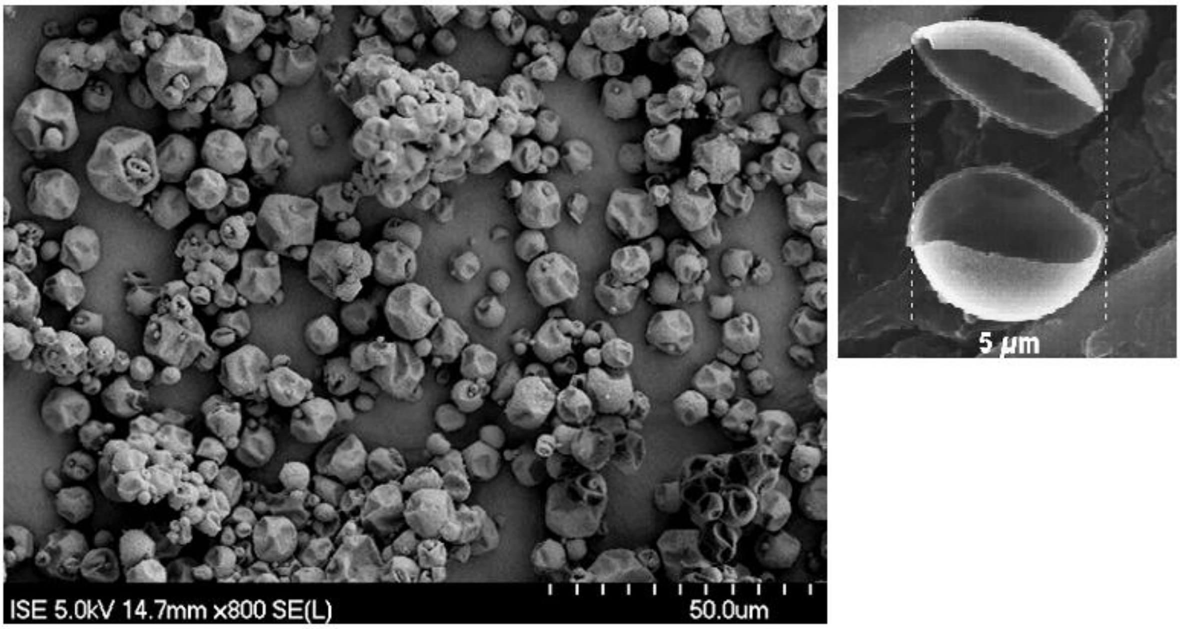

Figure 24: Electron microscope image of many capsules (picture: FhG-ISE) and an opened microcapsule [63].

The availability of commercial PCM, PCM composite materials and encapsulated PCM is crucial to the development and commercialization of PCM applications. The reason is that from a customers point of view, only commercial PCM, PCM composite materials and encapsulated PCM have *defined properties*, a *warranty*, a *fixed price*, and can be *delivered in a given time*. From a supplier point of view, the size of the potential market of a PCM, PCM composite, or encapsulated PCM is also important. Both views determine what is commercially available.

The availability of commercial PCM, PCM composite materials, and encapsulated PCM allows companies with no or little knowledge on PCM to use this technology in their own products via a modular approach.Thus, for example, encapsulated PCM can be commercialized by one company specialized on PCM technology, and many other companies can then integrate the encapsulated PCM in their products, without knowing much about PCM technology. A good example is ice packs, which are used by many consumers to keep food cold.

Table 12 shows some commercial PCMs available in the market with their thermo physical properties given by companies producing them, while table 13 shows a list with the current companies that commercially produce PCMs, their website addresses, and the temperature range for PCM they are producing.

Table 14: Commercial PCMs available in the market and their thermophysical properties [64]

PCM name	Type of product	Melting temperature (°C)	Heat of fusion (kJ/kg)	Density (kg/m³)	Source
SN33	Salt solution	-33	245	1,24	Cristopia
TH-31	n.a.	-31	131	n.a.	TEAP
SN29	Salt solution	-29	233	1,15	Cristopia
SN26	Salt solution	-26	268	1,21	Cristopia
TH-21	n.a.	-21	222	n.a.	TEAP
SN21	Salt solution	-21	240	1,12	Cristopia
STL-21	Salt solution	-21	240	1,12	Mitsubishi Chemical
SN-18	Salt solution	-18	268	1,21	Cristopia
TH-16	n.a.	-16	289	n.a.	TEAP
STL-16	n.a.	-16	n.a.	n.a.	Mitsubishi Chemical
SN15	Salt solution	-15	311	1,02	Cristopia
SN12	Salt solution	-12	306	1,06	Cristopia
STLN10	Salt solution	-11	271	1,05	Mitsubishi Chemical
SN10	Salt solution	-11	310	1,11	Cristopia
TH-10	n.a.	-10	283	n.a.	TEAP
STL-6	Salt solution	-6	284	1,07	Mitsubishi Chemical
SN06	Salt solution	-6	284	1,07	Cristopia
TH-4	n.a.	-4	286	n.a.	TEAP
STL-3	Salt solution	-3	328	1,01	Mitsubishi Chemical
SN03	Salt solution	-3	328	1,01	Cristopia
ClimSel C 7	n.a.	7	130	n.a.	Climator
RT5	Paraffin	9	205	n.a.	Rubitherm GmbH
ClimSel C 15	n.a.	15	130	n.a.	Climator
ClimSel C 23	Salt solution	23	148	1,48	Climator
RT25	Paraffin	26	232		Rubitherm GmbH
STL27	Salt solution	27	213	1,09	Mitsubishi Chemical
S27	Salt solution	27	207	1,47	Cristopia
RT30	Paraffin	28	206	n.a.	Rubitherm GmbH
TH29	Salt solution	29	188	n.a.	TEAP
ClimSel C 32	Salt solution	32	212	1,45	Climator
RT40	Paraffin	43	181	n.a.	Rubitherm GmbH
STL47	Salt solution	47	221	1,34	Mitsubishi Chemical
ClimSel C 48	n.a.	48	227	1,36	Climator
STL52	Salt solution	52	201	1,3	Mitsubishi Chemical
RT50	Paraffin	54	195	n.a.	Rubitherm GmbH
STL55	Salt solution	55	242	1,29	Mitsubishi Chemical
TH58	n.a.	58	226	n.a.	TEAP
ClimSel C 58	n.a.	58	259	1,46	Climator

RT65	Paraffin	64	207		Rubitherm GmbH
ClimSel C 70	n.a.	70	194	1,7	Climator
PCM72	Salt solution	72	n.a.	n.a.	Merck KgaA
RT80	Paraffin	79	209	n.a.	Rubitherm GmbH
TH89	n.a.	89	149	n.a.	TEAP
RT90	Paraffin	90	197	n.a.	Rubitherm GmbH
RT110	Paraffin	112	213	n.a.	Rubitherm GmbH

n.a.: not available

Sources:

Merck KgaA: J.Heckenkamp, H.Baumann, Latentwarmespeicher, Sonderdruck aus Nachrichten 11 (1997) 1075–1081

Cristopia: Available from <www.cristopia.com>

TEAP: Available from <www.teappcm.com>

Mitsubishi Chemical: H.Kakiuchi, Mitsubishi Chemical Corporation, 2002. <climator.com>

Rubitherm GmbH: Available from www.rubitherm.de

Table 15: Some of the commercial PCMs manufacturers in the world [65]

Manufacturer	**Web-addresse**	**PCM temperature range**	**Number of PCMs listed**
RUBITHERM	(www.rubitherm.de)	from -3°C to 100°C	29
Cristopia	(www.cristopia.com)	from -33°C to 27°C	12
TEAP	(www.teappcm.com)	from -50°C to 78°C	22
Doerken	(www.doerken.de)	from -22°C to 28°C	2
Mitsubishi Chemical	(www.mfc.co.jp)	from 9,5°C to 118°C	6
Climator	(www.climator.com)	from -18°C to 70°C	9
EPS Ltd	(epsltd.co.uk)	from -114°C to 164°C	61
Merck			

Table 16: Som of the comercials PCM with their properties

Name	Phase change temperature (°C)	Type	Density solid (kg/m³)	Density liquid (kg/m³)	Latent heat capacity (kJ/kg)	Volumetric heat capacity (MJ/m³)	Specific heat capacity (kJ/kgK)	Viscosity (mm²/s)	Thermal conductivity (W/mK)	Volume expansion (%)	Source
RT4	-4	Organic	880	760	179	147		17,81	0,2	16	RUBITHERM
RT3	4	Organic	880	770	198	163		17,57	0,2	14	RUBITHERM
RT60	60	Organic	880	770	144	119		37,5	0,2	14	RUBITHERM
RT82	82	Organic	880	770	176	145		45,45	0,2	14	RUBITHERM
RT27	27	Organic	880	760	184			26,32	0,2	16	RUBITHERM
RT50	49	Organic	880	760	168			31,2	0,2	16	RUBITHERM
RT65	65	Organic	880	780	152			38,96	0,2	12	RUBITHERM
SP21E	21	hydrated		1500	160	240	2		0,6	3	RUBITHERM
S89	89	Salt hydrated		1550	151	234	2,48		0,68		PCM products
C70	70	Salt hydrated		1400	283	396	3,6		0,5		Climator
C58	58	Salt hydrated		1460	288	421	1,8		0,6		Climator

5 Mathematical model

5.1 Introduction

In this chapter a mathematical model of the energy balance during the energy storage (charge) and energy discharge from the PCM material is presented.

The storage unit is a cylindrical tank with PCM tube (Fig.25). The heat transfer process between the HTF and the PCM tube during charging and discharging processes is analysed. During the charging process, the HTF is flowing around the tube in the axial direction. During the discharging process, the cold water is flowing in the axial direction around the tube. When HTF runs through the storage system, heat is transferred between the HTF and PCM through the tube. In charge mode, the HTF is hotter that the PCM and in discharge mode the PCM is hotter than the HTF. During discharging process, the cold water temperature is fixed throughout the discharging process.

The model is based on the following simplifications:

- The PCM is treated as being completely immobile as all natural convection effects are neglected by ignoring any gravitational forces applying constant values for liquid PCM density,
- the PCM is homogeneous and isotropic,
- the HTF is incompressible and it can be considered as a Newtonian fluid,
- inlet velocity and inlet temperature of the HTF are constant,
- initial temperature of the latent heat storage unit is uniform and the PCM is in the solid phase for melting or in the liquid phase for solidification,
- the problem is axisymmetric,
- thermophysical properties of the HTF and the PCM are constant,
- HTF flow is axial,
- Inlet velocity and temperature are supposed to be known,
- Initial temperature of PCM is also supposed to be known.

5.2 Simplified algorithm for calculation of PCM temperature

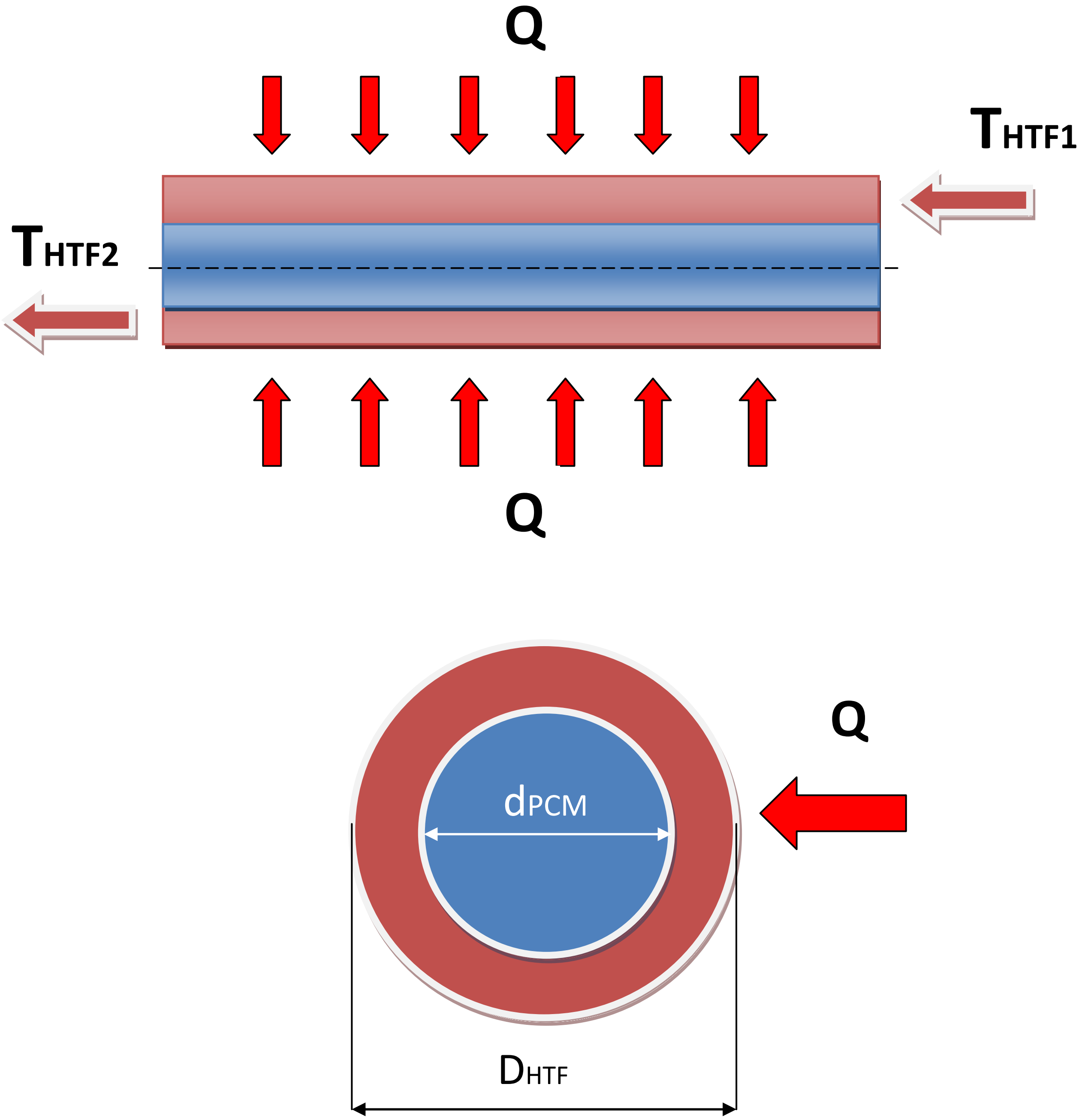

Figure 25: PCM tube in tank

A long PCM cylinder is placed in a duct. The duct is filled with HTF (hot water). The HTF is moving in axial direction, along PCM.

Heat transfer from the water to the PCM-wall (convection only):

$$\dot{Q} = \dot{m}c_{pHTF}\Delta T_{HTF} \tag{7}$$

$$\Delta T_{HTF} = T_{HTF1} - T_{HTF2} \tag{8}$$

Heat transfer in PCM (conduction only;
no temperature change in circumferential and axial direction assumed):

1) **Solid state:**

$$T_{PCM} = \left[T_{PCM,0}, T_{melt}\right] \tag{9}$$

$\gamma = 0$ liquid volume fraction (solid state)

The 1-D model is obtained from Eqs (10) and (11) for the solid phase by considering that the heat conduction occurs only along the radial direction and heat conduction along the axial direction is neglected. Moreover, the thermal losses to the ambient are assumed to be zero. And the temperature of the PCM is calculated from Eqs. (12) for the solid phase.

The heat released by the flowing HTF is equal to the energy transfer causing the temperature change in PCM, which can be written as:

$$\rho_s V c_{p,s} \frac{dT_{PCM}}{dt} = \dot{Q} \tag{10}$$

Where: ρ_s is density of solid phase (kg/m^3), V is volume of the PCM tube (m^3), $c_{p,s}$ is specific heat of solid phase (J/kgK), $\dot{Q}$ is the amount of thermal energy stored or released from sensible heta in time (J/s).

Introducing a finite-difference approximation of the time derivative, and substituing eq. (7) for *Q* the above equation can be written in the following form:

$$\rho_s V c_{p,s} \frac{T_{PCM}{}^{m+1} - T_{PCM}{}^{m}}{\Delta t} = Q \doteq \dot{m}c_{p,HTF}(T_{HTF1} - T_{HTF2}) \tag{11}$$

or

$$T_{PCM^{m+1}} = T_{PCM^{m}} + \frac{\dot{m}\, c_{p,HTF}(T_{HTF1} - T_{HTF2})}{\rho_s V c_{p,s}} \Delta t \tag{12}$$

Where: m is index of the time step (-), Δt is initial time step (s), $\dot{m}$ is mass flow of water (HTF) (kg/s), $c_{p,HTF}$ is specific heat of water (J/kgK), T_{HTF1} is temperature of water (HTF) at inlet (K), T_{HTF2} is temperature of water (HTF) at outlet (K), ρ_s is density of solid phase (kg/m^3), V is volume of the PCM tube (m^3), $c_{p,s}$ is specific heat of solid phase (J/kgK), $T_{PCM^{m}}$ is temperature of PCM in tim step m (K), $T_{PCM^{m+1}}$ is temperature of PCM in tim step m+1 (K).

2) Mushy state

$$T_{PCM} = T_{melt} \tag{13}$$

After the PCM temperature reaches the phase-change level, eq. (13), the energy supplied to the PCM is stored in the material in the form of latent heat. The change of the enthalpy of PCM is caused by the heat obtained from PCM:

$$\frac{dH}{dt} = \dot{Q} \tag{14}$$

$$\frac{d(\rho V h)}{dt} = \dot{Q} \tag{15}$$

$$\rho_{PCM} V_{PCM} \frac{d\gamma h}{dt} = \dot{Q} \tag{16}$$

$$\rho_{PCM} V_{PCM} \frac{d\left(c_{p,PCM} T + \gamma h_L\right)}{dt} = \dot{Q} \tag{17}$$

Where: h_L is the latent heat of PCM (J/kg), ρ_{PCM} is density of PCM (kg/m^3), V_{PCM} is volume of the PCM tube (m^3), $c_{p,PCM}$ is specific heat of PCM (J/kgK), γ is liquid volume fraction (-).

$$\rho_{PCM} V_{PCM} \left[c_{p,PCM} \frac{dT}{dt} + \frac{d\gamma h_L}{dt}\right] = \dot{Q} \tag{18}$$

There is no temperture change in mushy phase and the first derivative of the temperature is zero:

$$\frac{dT}{dt} = 0 \tag{19}$$

$$\rho_{PCM} V_{PCM}\, h_L \frac{d\gamma}{dt} = \dot{Q} \tag{20}$$

The liquid fraction gamma is calculated from Eqs. (21):

$$\gamma^{m+1} = \gamma^m + \frac{\dot{Q}}{\rho_{PCM} V_{PCM} h_L} \Delta t \tag{21}$$

and should be in the range $\gamma = [0,1]$

3) Liquid state

$$T_{PCM} = [T_{melt,} \propto] \tag{22}$$

The 1-D model is obtained from Eqs (23) and (24) for the liquid phase by considering that the heat conduction occurs only along the radial direction and heat conduction along the axial direction is neglected. Moreover, the thermal losses to the ambient are assumed to be zero. And the temperature of the PCM is calculated from Eqs. (25) for the liquid phase.

Similarly, as in the case of the heat transfer in the solid state, the heat exhanged with HTF is affecting the sensible heat of PCM.

$\gamma = 1$ liquid volume fraction (liquid state)

$$\rho_L V c_{p,L} \frac{dT_{PCM}}{dt} = \dot{Q} \tag{23}$$

$$\rho_L V c_{p,L} \frac{T_{PCM^{m+1}} - T_{PCM^m}}{\Delta t} = Q \doteq \dot{m} c_{p,HTF}(T_{HTF1} - T_{HTF2}) \tag{24}$$

$$T_{PCM^{m+1}} = T_{PCM^m} + \frac{\dot{m}\, c_{p,HTF}(T_{HTF1} - T_{HTF2})}{\rho_L V c_{p,L}} \Delta t \tag{25}$$

Where: ρ_L is density of liquid phase (kg/m^3), V is volume of the PCM tube (m^3), $c_{p,L}$ is specific heat of liquid phase (J/kgK).

5.3 The Results of Simulations

Assumptions applied for the dimension of the tube, tank, and characteristics of the phase change material (PCM) and hot water as the heat transfer fluid (HTF) were:

1) Diameter of the tube d_{PCM} = 0,05 [m]
2) Diameter of the tank D_{HTF} = 0,1 [m]
3) Hydraulic diametre d_h = 0,05 [m]
4) Lenhgt of the tube L = 1 [m]
5) Initial velocity of water (HTF) v_{water_inlet} = 1,50 [m/s]
6) Water inlet temperature T_{HTF1} = 70 [°C]
7) Water outlet temperature T_{HTF2} = 30 [°C]
8) Melting temperature of the PCM $T_{melt,PCM}$ = (28, 29, 42, 48 and 60) [°C] for different materials.
9) The mass flow of water (HTF) $\dot{m}_{water,HTF}$ = 2,94 [kg/s]
10) Mass of the PCM tube m_{PCM} = 262,19 [kg]
11) Spesific heat capacity of water $c_{p,water}$ = 4200 [J/kgK]
12) Spesific heat capacity of PCM for solid phase $c_{p,PCM,Solid}$ (depending on the type of PCM) [J/kgK]
13) Spesific heat capacity of PCM for liquid phase $c_{p,PCM,Liquid}$ (depending on the type of PCM) [J/kgK]
14) Density of wate (HTF) $\rho_{water,HTF}$ = 1000 [kg/m^3]
15) Density of PCM ρ_{PCM} (depending on the type of PCM) [kg/m^3]
16) Mass of the water sensible $m_{water,sensible}$ = 157 [kg]
17) Intial time step Δt_{in} = 1 or 2 [s]

5.3.1 Temperature change of the PCM and heat stored for PCM NaS_2O_3

Figure 25 shows temperature profil change of PCM (NaS_2O_3) in time melting temperature of PCM is 48°C.

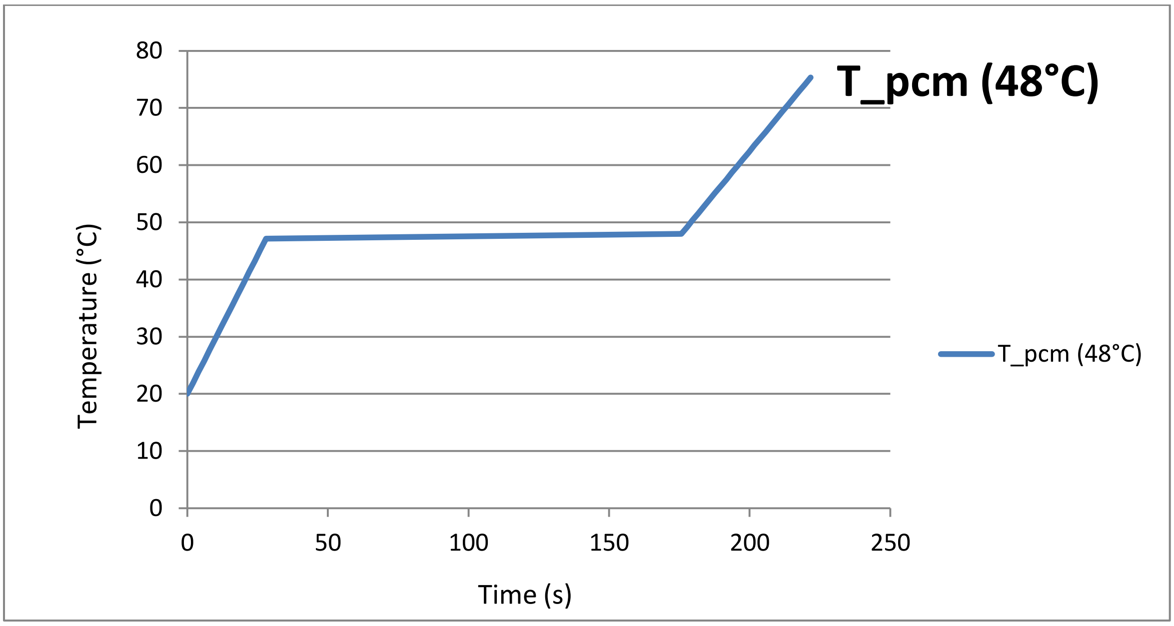

Figure 26: Temperature profil cahange for PCM NaS_2O_3 for initial time step 2s

The fig. 26 shows the change in temperature PCM (NaS_2O_3) in time for the initial time step of 1 s, melting temperature of PCM is 48°C.

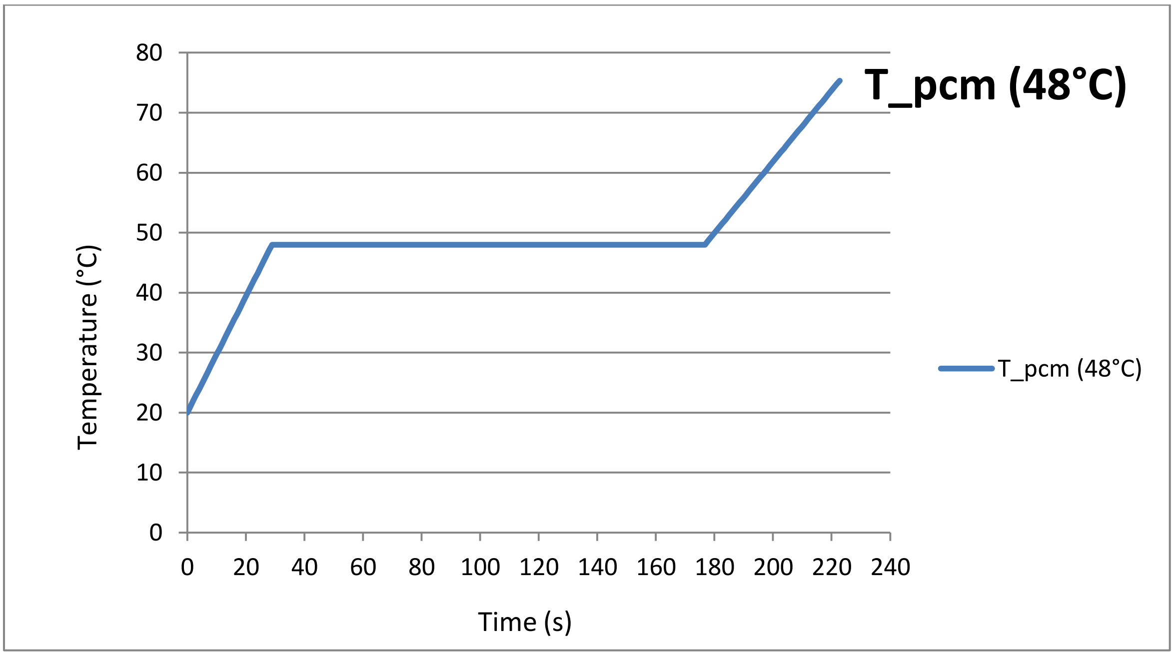

Figure 27: Temperture profil change for PCM NaS_2O_3 for initial time step 1s

Figure 27 shows the amount of heat stored during the time (latent heat) for PCM NaS_2O_3 and the amount of heat stored (sensible heat) with water as a medium for energy storage instead of PCM.

It is clearly seen that much more energy is stored through the latent heat during the phase change of NaS_2O_3 than energy stored trough sensible heat.

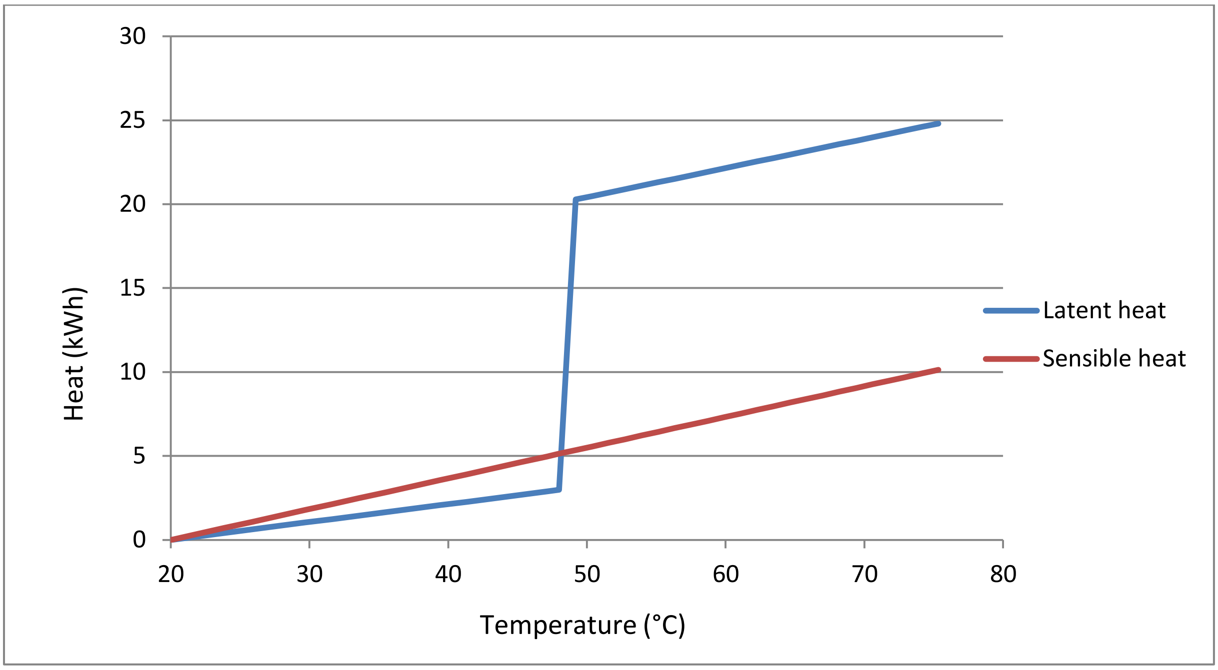

Figure 28: Heat stored during the tim with PCM (NaS_2O_3) and heat stored with water as storage medium

5.3.2 Temperature change of the PCM and heat stored for PCM $CaCl_2$

Figure 28 shows the temperature profil change of PCM ($CaCl_2$) in time, melting temperature of PCM is 29°C.

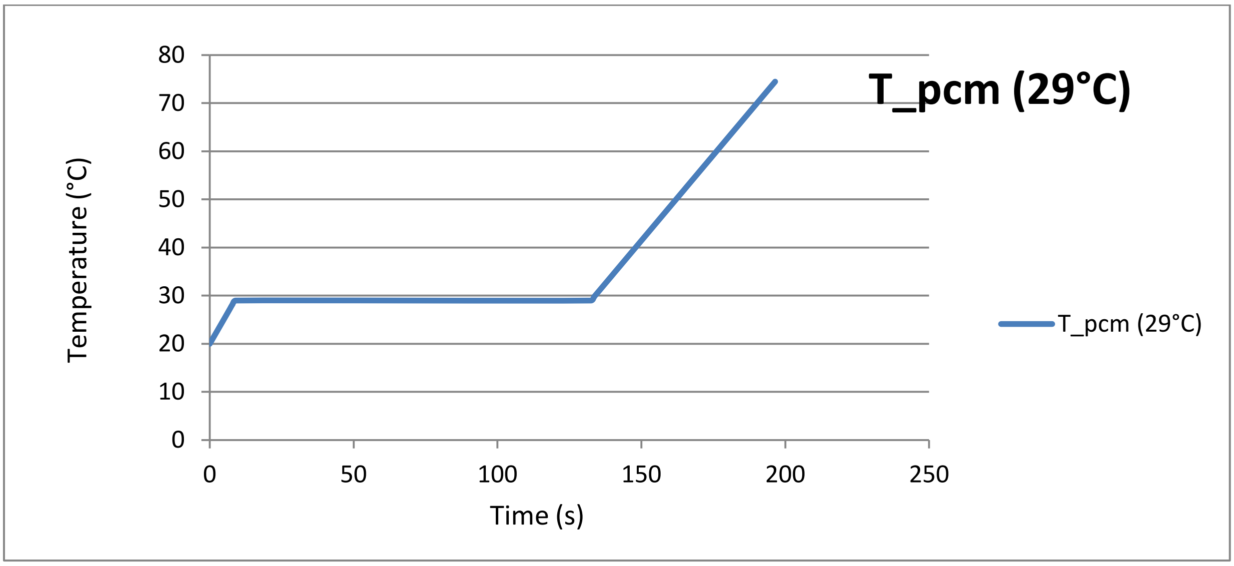

Figure 29: Temperature profil change for PCM $CaCl_2$ with initial tim step 1

Figure 29 shows the amount of heat stored during the time (latent heat) for PCM $CaCl_2$ and the amount of heat stored (sensible heat) with water as a medium for energy storage instead of PCM.

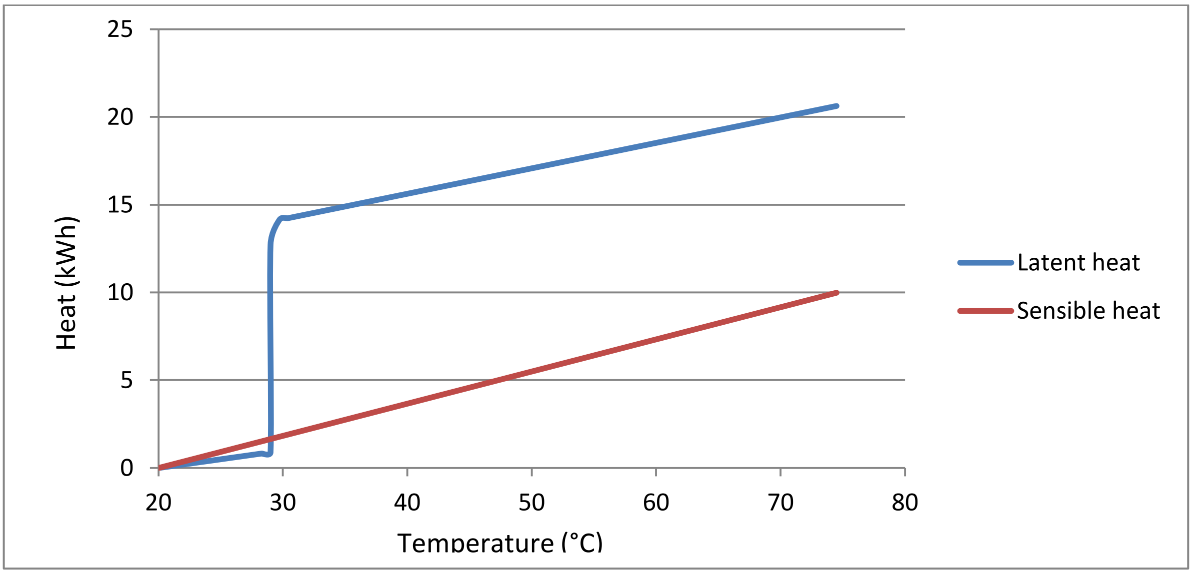

Figure 30: Heat stored during the tim with PCM (CaCl2) and heat stored with water as storage medium

5.3.3 Temperature change of the PCM and heat stored for PCM $C_{18}H_{38}$

Figure 30 shows the temperature profil change of PCM ($C_{18}H_{38}$) in time for the initial time step of 1 s, melting temperature of PCM is 28°C.

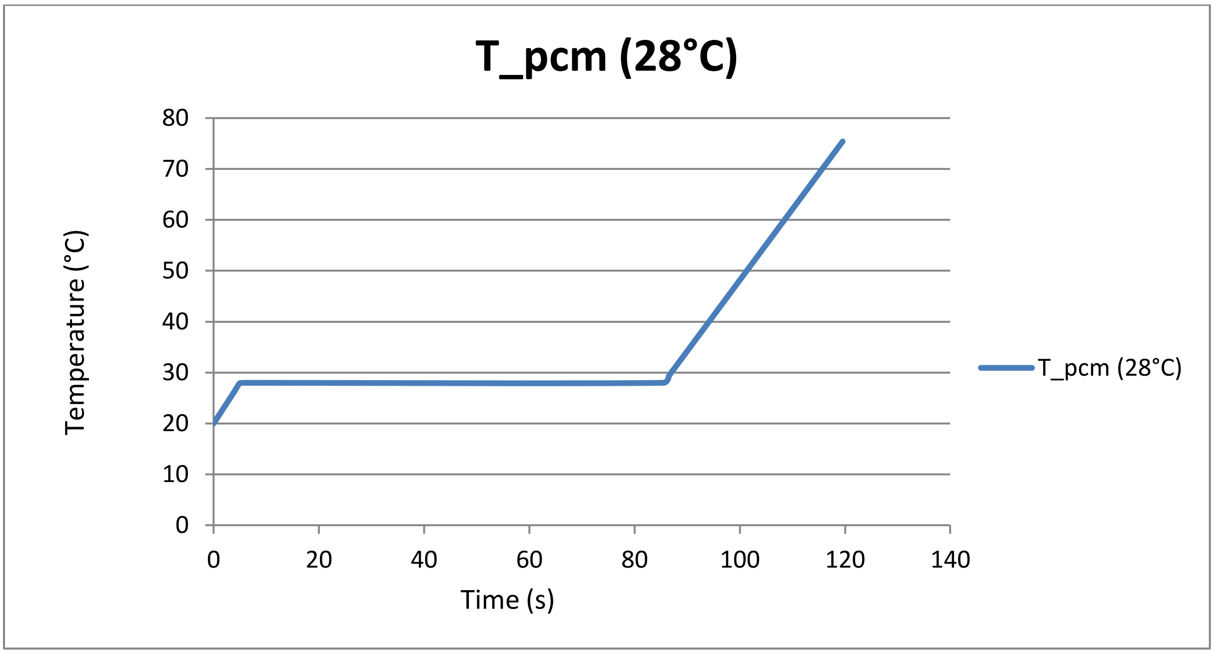

Figure 31: Temperature profil cahange for PCM $C_{18}H_{38}$ for initial time step 1s

Figure 31 shows the amount of heat stored during the time (latent heat) for PCM $C_{18}H_{38}$ and the amount of heat stored (sensible heat) with water as a medium for energy storage instead of PCM.

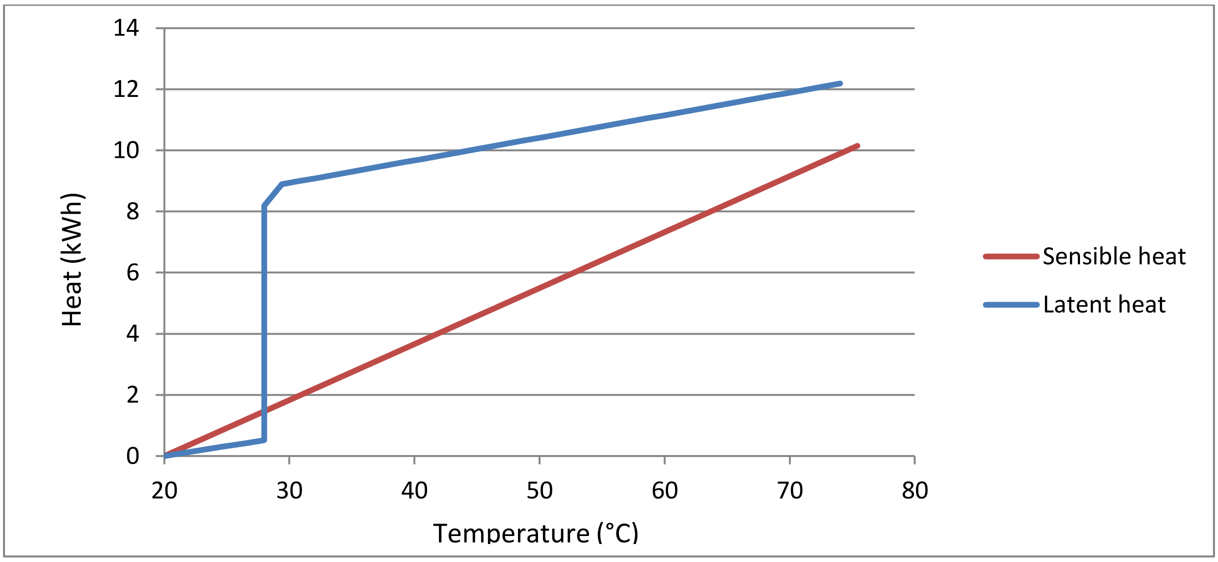

Figure 32: Heat stored during the tim with PCM ($C_{18}H_{38}$) and heat stored with water as storage medium

5.3.4 Temperature change of the PCM and heat stored for Comercial PCM RT42

Figure 32 shows the temperature profil change of PCM (Comercial PCM RT42) in time for the initial time step of 1 s, melting temperature of PCM is 42°C.

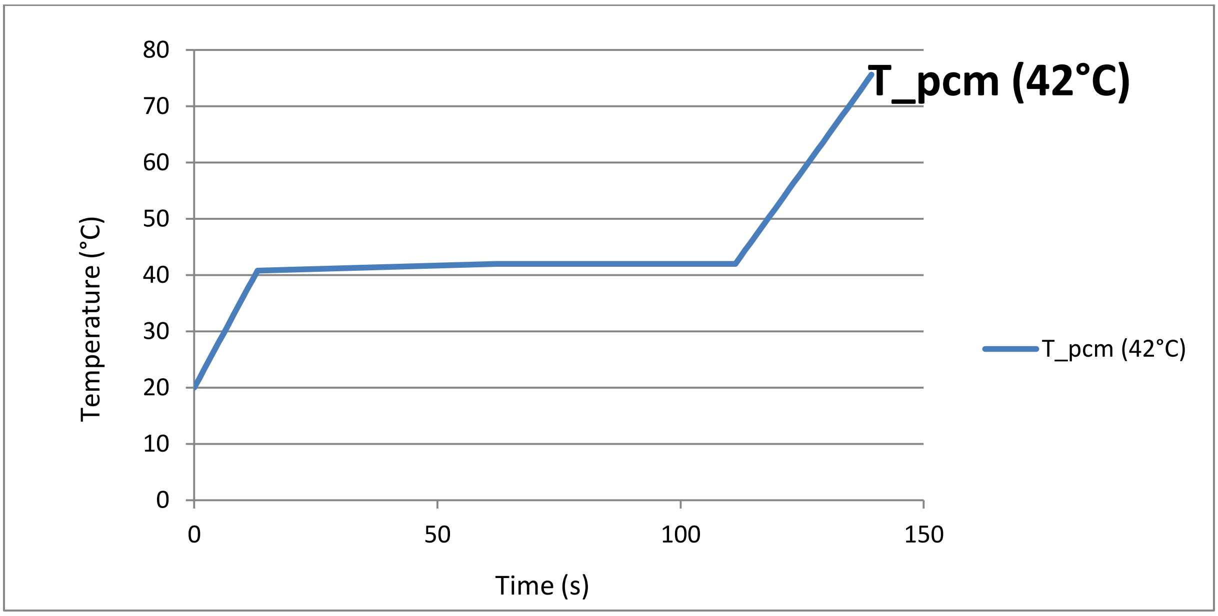

Figure 33: Temperature profil cahange for Comercial PCM RT42 for initial time step 1s

Figure 33 shows the amount of heat stored during the time (latent heat) for Comercial PCM RT42 and the amount of heat stored (sensible heat) with water as a medium for energy storage instead of PCM.

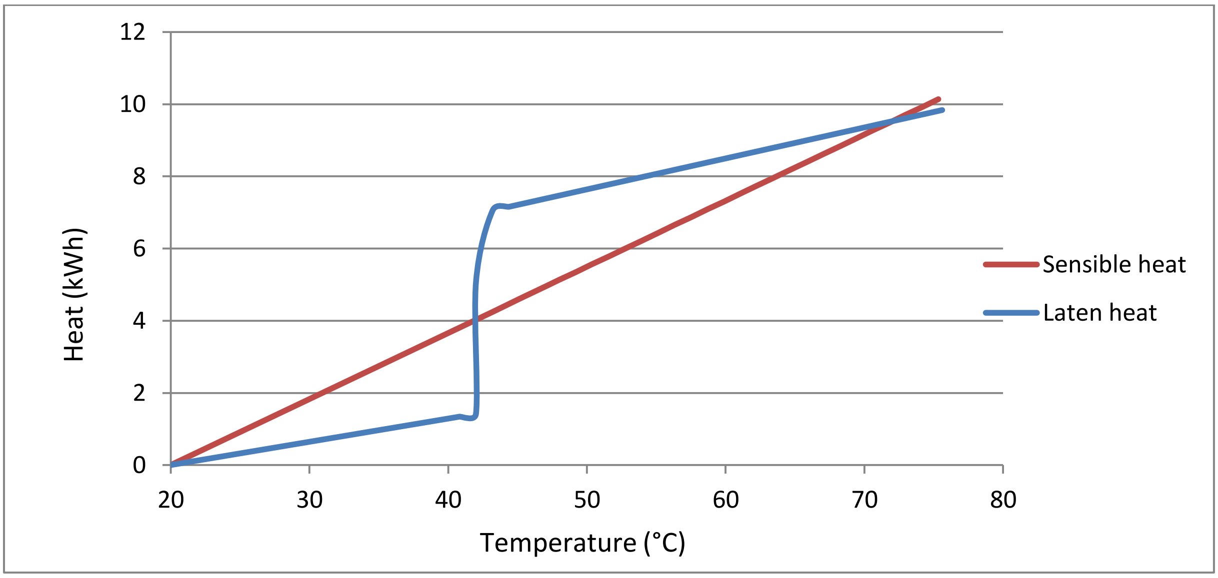

Figure 34: Heat stored during the tim with Comercial PCM RT42 and heat stored with water as storage medium

5.3.5 Temperature change of the PCM and heat stored for Paraffin T_{melt}=60°C

Figure 34 shows the temperature profil change of PCM (Parraffin T_{melt}=60°C) in time for the initial time step of 1 s, melting temperature of PCM is 60°C.

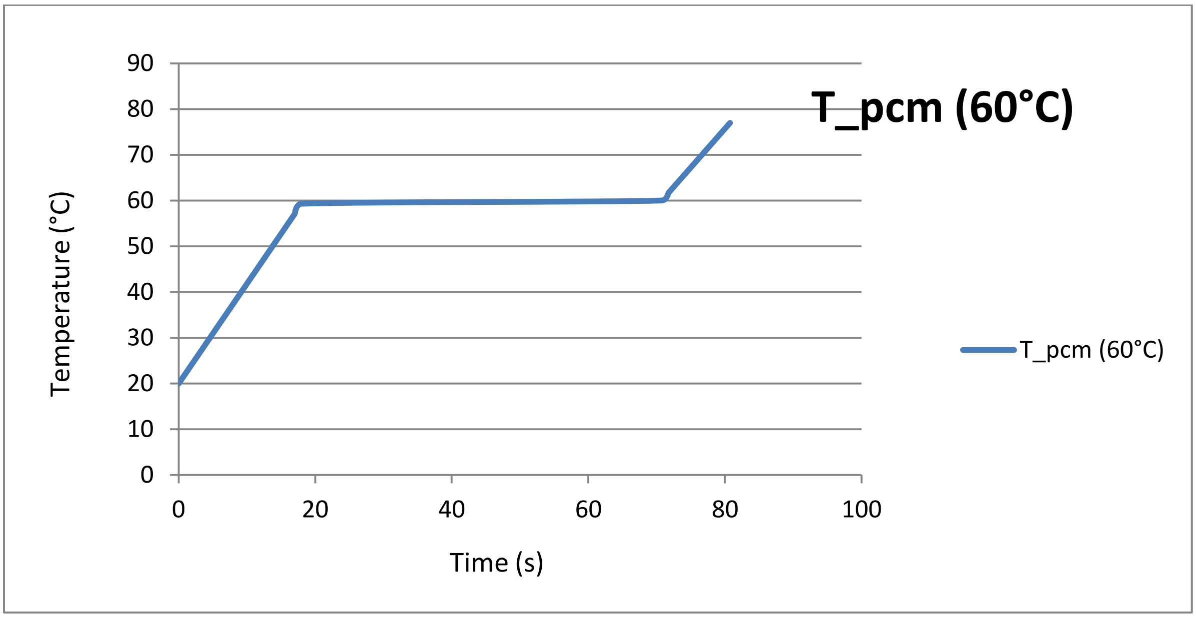

Figure 35: Temperature profil cahange for Parrafin PCM T_{melt}=60°C for initial time step 1s

Figure 35 shows the amount of heat stored during the time (latent heat) for Paraffin PCM T_{melt}=60°C and the amount of heat stored (sensible heat) with water as a medium for energy storage instead of PCM.

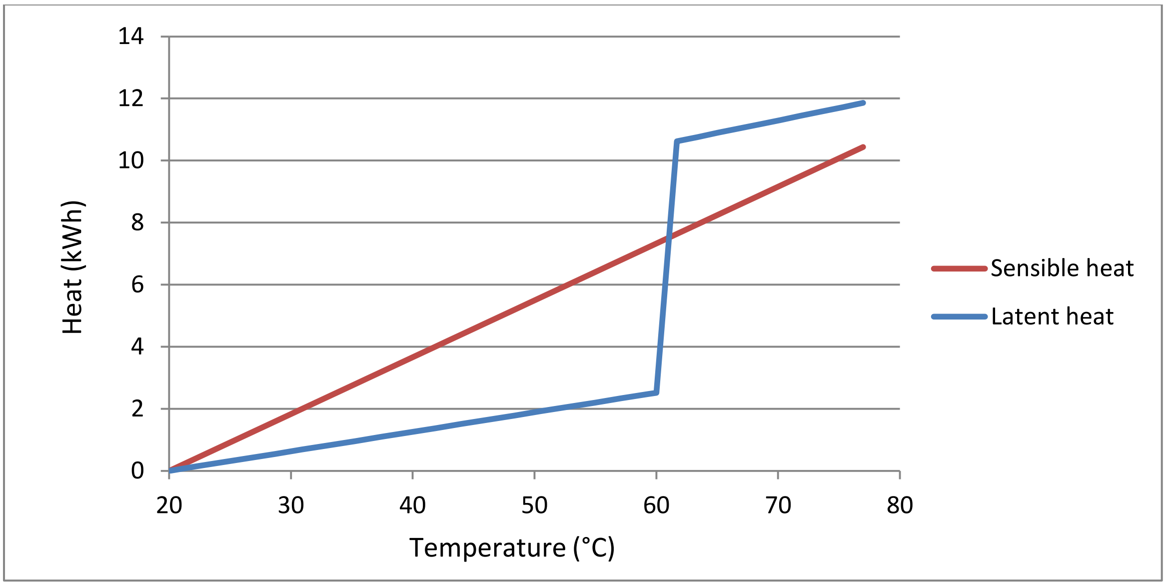

Figure 36: Heat stored during the tim with Paraffin PCM T_{melt}=60°C and heat stored with water as storage medium

5.3.6 Comparison of different phase-changing materials, the amount of stored energy

Figure 37 shows the theoretical energy storage capacity of the model, with an ambient temperature of 20 ˚C, for five different PCMs and sensible heat storage in water as a function of temperature. The vertical lines indicate the amount of energy stored in the phase change, and the diagonal lines indicate the amount of sensible energy stored. The sensible energy is only stored in the heat transferfluid for sensible heat storage in water, and stored in heat transfer fluid, PCM and module material for the latent heat storage. The calculations for this example are found in Excel file.

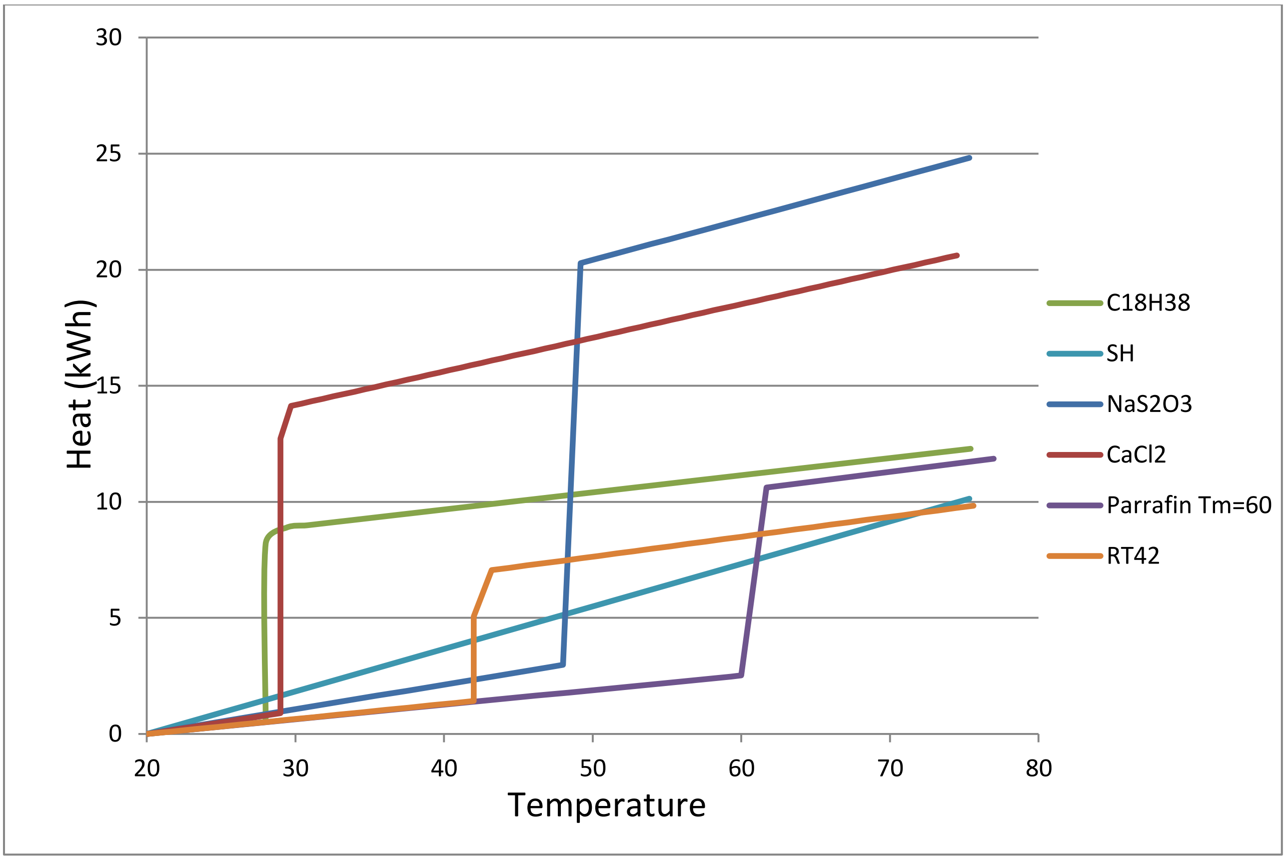

Figure 37: Comparison of different phase-change materials and the amount od stored energy

Figure 37 shows that all the PCMs except RT42 give a higher theoretical storage capacity than water between the melting point of the PCMs and 75 ˚C. The two chosen salt hydrates, $CaCl_2·6H_2O$ and $Na_2S_2O_3·5H_2O$, gives a much higher theoretical storage capacity than the two chosen organic PCMs, paraffin T_m = 60 °C and $C_{18}H_{38}$. The two salt hydrates have a higher latent heat of fusion and specific heat capacity inregards to volume compared to the organic PCMs.

In case of phase change material RT42 the sensible heat storage with water is higher the latent energy stored with PCM RT 42 because small latetn heat of fusion of chosen material (RT42).

The specific heat capacity of the solid phase of the PCM is lower than for the liquid phase. This means that with a low melting point, the amount of sensible energy stored in the PCM will increase.

The storage temperature for both latent and sensible heat storage is crucial for the heat loss to the environment. One of the advantages of storing energy latent is that it is possible to store larger amounts of energy at a lower temperature than with sensible heat storage. Another advantage is that for longer storage periods the temperature of the tank will remain at the melting point of the PCM until all the latent energy is released.

6 Algorithm for for more detailed calculation of PCM temperature

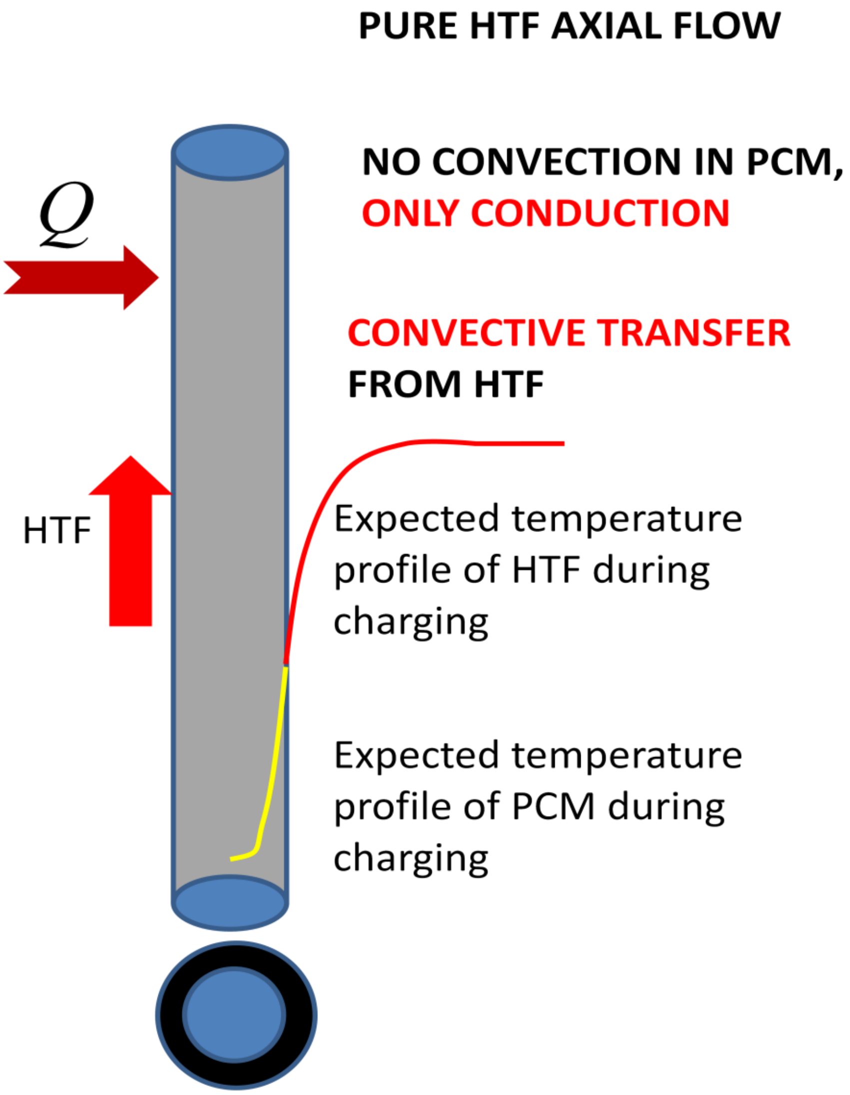

Figure 38: PCM Tube

Previous analysis assumes that the PCM temperature is uniform wihtin the entire PCM. Such a procedure is acceptable for a fast overall analysis of the charging/discharing time. However, it is clear that the PCM temperature varies between the wall surface and the PCM interior due to heat conduction. In order to analyze this, it is necessary to estimate the temperature at the PCM wall surface.

Heat transfer from the water to the PCM-wall (convection only):

$$dQ = \dot{m}c_p dT \tag{26}$$

$$Q = \dot{m}c_p(T_2 - T_1) \tag{27}$$

$$Q = \alpha A(T_{\text{mean}} - T_{\text{wall}}) \tag{28}$$

Where α is the heat transfer coefficient (W/m^{2}K), Tx is water temperature on specific place x (K), Tmean is mean water temperatura (K), Twall is temperature of water on wall (K), Q is the amount of thermal energy stored or released from sensible heta (J), $\dot{m}$ is mass flow of water (kg/s), A is specific area (m^2).

$$T_{\text{mean}} = \frac{T_1 - T_2}{\ln\frac{T_1 - T_{\text{wall}}}{T_2 - T_{\text{wall}}}} \text{ (29)}$$

From the eqs. (27-29) one obtains Twall.

$$\alpha = Nu\,\lambda/d_{\text{PCM}} \tag{29}$$

$$Re = \frac{\rho_{HTF} v_{inlet,HTF} d_{PCM}}{\mu_{HTF}} \tag{30}$$

Nusselt number for the flow through a tube [66]:

$$Nu_1 = \frac{(\varepsilon/8)RePr}{1 + 12{,}7\sqrt{\varepsilon/8}\left(Pr^{2/3} - 1\right)}\left\{1 + \ (d_h/L)^{2/3}\right\} \tag{31}$$

Additional parameter:

$$\varepsilon = (1{,}8\log_{10} Re - 1{,}5)^2 \tag{32}$$

Hydraulic diameter:

$$d_h = D_{HTF} - d_{PCM} \tag{33}$$

$$\frac{Nu_m}{Nu_1} = 0{,}86(D_{HTF}/d_{PCM})^{-0{,}16} Nu1 \tag{34}$$

Final Nusselt number for the flow trough tube:

$$Nu = Nu_m \left(\frac{Pr}{Pr_w}\right)^{0{,}11} \tag{35}$$

$$A = d_{\mathrm{PCM}}\, \pi\, L \tag{36}$$

From eqs. (26)-(36), T_{wall} can be obtained.

Heat transfer in PCM (conduction only;
no temperature change in circumferential and axial direction assumed):

The heat conducted through the PCM surface affects the temperature within the PCM:

$$\rho_{\mathrm{PCM}} V_{\mathrm{PCM}} c_{\mathrm{p,PCM}} \frac{T_{\mathrm{PCM}}{}^{m} - T_{\mathrm{PCM}}{}^{m-1}}{\Delta t} = \lambda \nabla T|_{\mathrm{wall}}\, d_{\mathrm{PCM}} \pi L \tag{37}$$

where the term on the right-hand side of the above equation represents the heat conduction, and λ is is the heat conduction coefficient (W/mK), L is length (m), ρ_{PCM} is density of PCM (kg/m^3), V_{PCM} is volume of the PCM tube (m^3), $c_{\mathrm{p,PCM}}$ is specific heat of PCM (J/kgK) d_{PCM} is diameter of PCM tube (m) T_{PCM^m} is temperature of PCM in tim step m (K), $T_{PCM}{}^{m-1}$ is temperature of PCM in tim step m-1 (K).

The simplest approximation of the temperature gradient NABLA T can be done using finite-diference approximation of the first order:

$$\nabla T = \frac{\partial T}{\partial r} \approx 2\,\frac{T_{\mathrm{wall}} - {T_{\mathrm{PCM}}}^{m-1}}{d_{\mathrm{PCM}}} \qquad \text{resulting in an explicit scheme} \tag{38}$$

Or

$$\nabla T = \frac{\partial T}{\partial r} \approx 2\,\frac{T_{\mathrm{wall}} - {T_{\mathrm{PCM}}}^{m}}{d_{\mathrm{PCM}}} \quad \text{resulting in an implicit scheme} \tag{39}$$

Eq. (38) combined either with eq. (39) or eq. (40) delivers the equation to be solved for T_{PCM}.

7 Conclusion

A review of the latent heat storage systems has been performed. A great progress has already been achieved with several models and laboratory devices which have been built. Nevertheless there is still work to do in order to reach to the commercialization of LHS devices.

Accumulation of energy in water is a well-known and well developed technology. Water is the most common media used for sensible energy storage. The reason for this is probably because of the high specific capacity and high density of water. To reduce the volume of the storage, utilization of latent energy storage has been proposed as a solution. Phase Change Materials are materials that have desirable phase change properties. Salt hydrates, parffins and eutectics have been found as the most promising PCMs. In the commercial market more than 100 PCMs are available at melting temperatures within the region of 0°C to 100 °C, with latent heat of fusion in the range of 100 to 300 kJ/kg.

A model for thermal energy storage has been developed for this paper. The model has been applied to four different Phase Change Materials, the two chosen salt hydrates, $CaCl_2{\cdot}6H_2O$ and $Na_2S_2O_3{\cdot}5H_2O$, gives a much higher theoretical storage capacity than the two chosen organic PCMs, paraffin $T_m = 60$ °C and $C_{18}H_{38}$. The two salt hydrates have a higher latent heat of fusion and specific heat capacity inregards to volume compared to the organic PCMs.

There are weaknesses to the PCM model. This model was built assuming that the PCM temperature is uniform wihtin the entire PCM. Such a procedure is acceptable for a fast overall analysis of the charging/discharing time. However, it is clear that the PCM temperature varies between the wall surface and the PCM interior due to heat conduction. In order to analyze this, it is necessary to estimate the temperature at the PCM wall surface.

Algorithm for for more detailed calculation of PCM temperature have been proposed in this thesis.

8 Further work

The model for the PCM storage has been difficult to apply in EXCEL. To improve the model and the general analysis for thermal energy storage solutions, it is referred to conduct the following:

1) PCM temperature varies between the wall surface and the PCM interior due to heat conduction. In order to analyze this, it is necessary to estimate the temperature at the PCM wall surface.
2) The model for assessing the available energy is based on a worst case scenario without heat loss from the tank. The model could be improved to calculate heat loss to environment.
3) During this thesis costs considerations have not been focus. Further work under this topic should include cost considerations.

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10 Appendix A: Commercial available PCMs

There are many different solutions for PCM on the marked already, some of the materials used is presented in the table below [67]:

Table 17: Commercial available PCM with mnelting temperatures between 0 and 100 °C and their properties [67]:

Name	Type	Phase change temperature [°C]	ρ [kg/m^3]	Latent heat capacity [kJ/kg]	Volumetric heat capacity[i] [MJ/m^3]	Specific heat capacity [kJ/kg*K]	Thermal conductivity [W/m*K]	Source
RT100	Organic	100	825	124	102		0,2	RUBITHERM[ii]
A95	Organic	95	900	205	185	2.2	0.22	PCMproducts
TH89	Hydrated salt	89	1550	145				Teaappcm
S89	Hydrated salt	89	1550	151	234	2,48	0,67	PCMproducts
PCM-HS89P	Hydrated salt	89	1540	180	277			savEnrg
S83	Hydrated salt	83	1600	141	226	2,31	0,62	PCMproducts
RT82	Organic	82	825	176	145		0,2	RUBITHERM
A82	Organic	82	850	155	132	2.21	0.220	PCMproducts
TH78	Hydrated salt	78	1800	240				Teaappcm
S72	Hydrated salt	72	1666	127	212	2,13	0,58	PCMproducts
TH70	Hydrated salt	70	1800	230				Teaappcm
C70	Hydrated salt	70	1400	283	396	3,6	0,5	Climator
A70	Organic	70	890	173	154	2.2	0.230	PCMproducts
TH68	Hydrated salt	68	1800	220				Teaappcm

RT65	Organic	65	830	152	126		0,2	RUBITHERM
RT62	Organic	62	830	146	121		0,2	RUBITHERM
RT60	Organic	62	825	144	119		0,2	RUBITHERM
A62	Organic	62	910	145	132	2.2	0.22	PCMproducts
A60	Organic	60	910	145	132	2.22	0.22	PCMproducts
TH58	Hydrated salt	58	1400	220				Teaappcm
S58	Hydrated salt	58	1505	145	218	2,55	0,69	PCMproducts
RT58	Organic	58	825	178	147		0,2	RUBITHERM
PCM-HS58P	Hydrated salt	58	1290	250	323			savEnrg
C58	Hydrated salt	58	1460	288	421	1,8	0,6	Climator
A58	Organic	58	910	132	120	2.22	0.22	PCMproducts
RT55	Organic	55	825	172	142		0,2	RUBITHERM
A55	Organic	55	905	135	122	2,22	0,22	PCMproducts
PCM-OM53P	Organic*	53	860	192	165			savEnrg
A53	Organic	53	910	130	118	2,22	0,22	PCMproducts
S50	Hydrated salt	50	1601	100	160	1,59	0,43	PCMproducts
TH48	Hydrated salt	48	1400	220				Teaappcm
C48	Hydrated salt	48	1360	180	245	3,6	0,6	Climator
S46	Hydrated salt	46	1587	210	333	2,41	0,45	PCMproducts
PCM-OM46P	Organic*	46	860	245	211			savEnrg

TH45	Hydrated salt	45	1400	220				Teaappcm
S44	Hydrated salt	44	1584	100	158	1,61	0,43	PCMproducts
RT42	Organic	42	820	174	143		0,2	RUBITHERM
A42	Organic	42	905	105	95	2,22	0,21	PCMproducts
TH40	Hydrated salt	40	1400	220				Teaappcm
A39	Organic	39	900	105	95	2,22	0,22	PCMproducts
PCM-OM37P	Organic*	37	880	218	192			savEnrg
TH36	Hydrated salt	36	1400	220				Teaappcm
S34	Hydrated salt	34	2100	115	242	2,1	0,52	PCMproducts
PCM-HS34P	Hydrated salt	34	1850	150	278			savEnrg
TH32	Hydrated salt	32	1400	220				Teaappcm
S32	Hydrated salt	32	1460	200	292	1,91	0,51	PCMproducts
C32	Hydrated salt	32	1420	162	230	3,6	0,6	Climator
A32	Organic	32	845	130	110	2,2	0,21	PCMproducts
RT31	Organic	31	820	169	139		0,2	RUBITHERM
S30	Hydrated salt	30	1304	190	248	1,90	0,48	PCMproducts
TH29	Hydrated salt	29	1500	175				Teaappcm
PCM-HS29P	Hydrated salt	29	1550	190	295			savEnrg
Latest	Hydrated	29	1500	188			1	Teaappcm

29	salt							
RT28HC	Organic	28	825	245	202		0,2	RUBITHERM
DELTA-cool 28	Hydrated salt	28	1550	188	291	2,2	0,56	Dörken
C28	Hydrated salt	28	1420	162	230	3,6	0,6	Climator
A28	Organic	28	789	155	122	2,22	0,21	PCMproducts
TH27	Hydrated salt	27	1500	175				Teaappcm
S27	Hydrated salt	27	1530	183	280	2,20	0,54	PCMproducts
RT27	Organic	27	820	184	151		0,2	RUBITHERM
AC27	Eutectic	27		185				Cristopa
A26	Organic	26	790	150	119	2,22	0,21	PCMproducts
S25	Hydrated salt	25	1530	180	275	2,2	0,54	PCMproducts
Latest 25	Hydrated salt	25	1500	188			1	Teaappcm
A25	Organic	25	785	150	118	2,26	0,18	PCMproducts
TH24	Hydrated salt	24	1500	175				Teaappcm
PCM-HS24P	Hydrated salt	24	1540	185	285			savEnrg
DELTA-cool 24	Hydrated salt	24	1550	158	245	2,2	0,56	Dörken
C24	Hydrated salt	24	1380	151	209	3,6	0,6	Climator
A24	Organic	24	790	145	115	2,22	0,18	PCMproducts
S23	Hydrated salt	23	1530	175	268	2,2	0,54	PCMproducts
A23	Organic	23	785	145	114	2,22	0,18	PCMproducts

PCM-HS22P	Hydrated salt	22	1540	185	285			savEnrg
A22	Organic	22	785	145	114	2,22	0,18	PCMproducts
TH21	Hydrated salt	21	1500	175				Teaappcm
S21	Hydrated salt	21	1530	170	260	2,2	0,54	PCMproducts
RT21	Organic	21	825	134	111		0,2	RUBITHERM
PCM-OM21P	Organic	21	1050	120	126			savEnrg
C21	Hydrated salt	21	1380	125	173	3,6	0,6	Climator
S19	Hydrated salt	19	1520	160	243	1,9	0,43	PCMproducts
TH18	Hydrated salt	18	1500	175				Teaappcm
S17	Hydrated salt	17	1525	160	244	1,9	0,43	PCMproducts
A17	Organic	17	785	150	118	2,22	0,18	PCMproducts
TH15	Hydrated salt	15	1400	175				Teaappcm
S15	Hydrated salt	15	1510	160	242	1,9	0,43	PCMproducts
A15	Organic	15	790	130	103	2,26	0,21	PCMproducts
S13	Hydrated salt	13	1515	160	242	1,9	0,43	PCMproducts
PCM-OM11P	Organic	11	1060	260	276			savEnrg
C10	Hydrated salt	10,5	1400	126	176	3,6	0,6	Climator
TH10	Hydrated salt	10	1400	170				Teaappcm

S10	Hydrated salt	10	1470	155	228	1,9	0,430	PCMproducts
PCM-OM06P	Organic	5.5	735	260	191			savEnrg
A9	Organic	9	775	140	109	2,16	0,21	PCMproducts
S8	Hydrated salt	8	1475	150	221	1,9	0,44	PCMproducts
PCM-OM08P	Organic	8	1050	190	200			savEnrg
A8	Organic	8	773	150	116	2,16	0,21	PCMproducts
TH7	Hydrated salt	7	1400	135				Teaappcm
TH7	Hydrated salt	7	1400	300				Teaappcm
S7	Hydrated salt	7	1700	150	255	1,85	0,4	PCMproducts
C7	Hydrated salt	7	1400	126	176	3,6	0,6	Climator
RT6	Organic	6	825	175	144		0,2	RUBITHERM
A6	Organic	6	770	150	116	2,17	0,21	PCMproducts
RT5HC	Organic	5	820	245	201		0,2	RUBITHERM
RT5	Organic	5	825	198	163		0,2	RUBITHERM
PCM-OM05P	Organic	5	770	198	223			savEnrg
TH4	Hydrated salt	4	1400	105				Teaappcm
RT4	Organic	4	825	182	150		0,2	RUBITHERM
A4	Organic	4	766	200	153	2,18	0,21	PCMproducts
RT3	Organic	3	825	198	163		0,2	RUBITHERM
A3	Organic	3	765	200	153	2,2	0,21	PCMproducts

A2	Organic	2	765	200	172	2,2	0,21	PCMproducts
PCM-HS00P	Hydrated salt	0	1010	290	152			savEnrg

*Organic compounds that are 100 % bio based raw materials which is non-tox and non-hazards

*1kWh=3.6MJ

*For RUBITHERM products the density is the average between liquid and solid densities