CH.2

PHASE CHANGE MATERIALS (PCM)

2.1 Introduction

In this chapter we will talk about phase change materials in details including definition of it.

We also give the reasons for choosing suitable PCM for our project and show how it works.

It is used in many applications which will be illustrated below. We also choose the suitable PCM for our application and point to the way of choosing it.

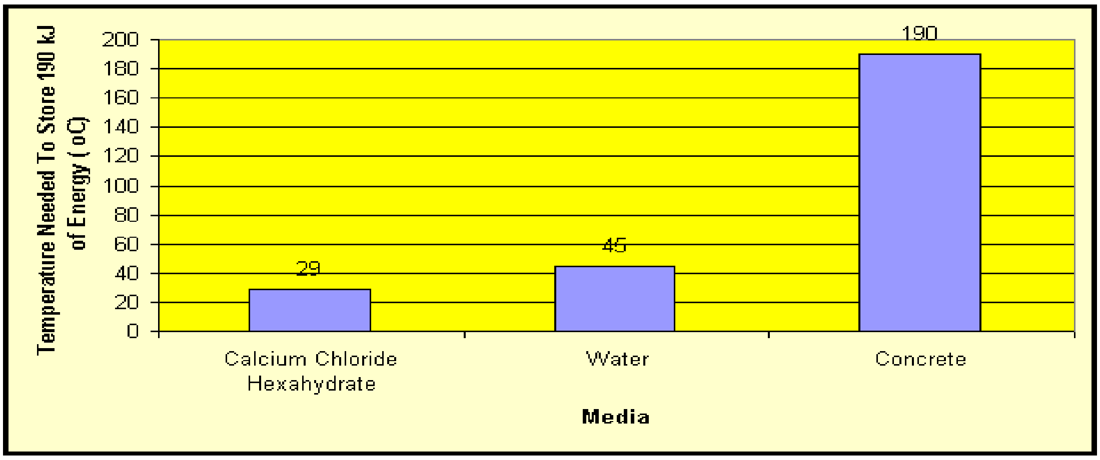
We mentioned to the usage of PCM in our project and how we try to use it in enhancing the efficiency and performance of our system.

We know that everything has its disadvantages so we have included this and make the available improvement and find the best solutions for enhancing the properties of our chosen PCM.

2.2 PCM Fundamentals and Technology Basics

Phase Change Materials (PCMs) are ideal products for thermal energy storage & considered as one of perfect enhancement solutions in many fields. This is because they store and release thermal energy during the process of melting & freezing (changing from one phase to another) so it is called latent heat energy storage systems. They use chemical bonds to store and release heat. When such a material freezes, it releases large amounts of energy in the form of latent heat of fusion, or energy of crystallization. Conversely, when the material is melted, an equal amount of energy is absorbed from the immediate environment as it changes from solid to liquid.

Thermal storage can be accomplished either by using sensible heat storage or latent heat storage. Sensible heat storage has been used for centuries by builders to store thermal energy, but a much larger volume of material is required to store the same amount of energy in comparison to latent heat storage. This fact is illustrated in the graph below. Calcium chloride hexahydrate is a PCM and at its melting point it can store/release 190 kJ of energy. To store the same amount of energy water would have to be heated to 45°C and concrete would have to be heated to 190°C.



During the same period of time, the amount of heat absorbed from 1 kg of water at 0^{o}C to convert into ice is about 225 KJ/kg & the other absorbed from 1 kg of ice when its temperature reduces from 0^{o}C to -1^{o}C is about 4.18 KJ/kg. So during the same period of time the amount of Latent heat is larger than the sensible heat for same amount of material.

The simplest, cheapest, and most effective phase change material is water/ice. Unfortunately, the freezing temperature of water is fixed at 0°C (32°F), which makes it unsuitable for the majority of energy storage applications. Therefore a number of different materials have been identified and developed to offer products that freeze and melt like water/ice, but at temperatures from the cryogenic range to several hundred degrees centigrade.

Initially, the solid–liquid PCMs behave like sensible heat storage (SHS) materials; their temperature rises as they absorb heat. Unlike conventional SHS, however, when PCMs reach the temperature at which they change phase (their melting temperature) they absorb large amounts of heat at an almost constant temperature. The PCM continues to absorb heat without a significant rise in temperature until all the material is transformed to the liquid phase. When the ambient temperature around a liquid material falls, the PCM solidifies, releasing its stored latent heat.

A large number of PCMs are available in any required temperature range from −5 up to 190°C. Within the human comfort range of 20° to 30°C, some PCMs are very effective. They store 5 to 14 times more heat per unit volume than conventional storage materials such as water, masonry or rock.

2.2.1 Characteristics and classification

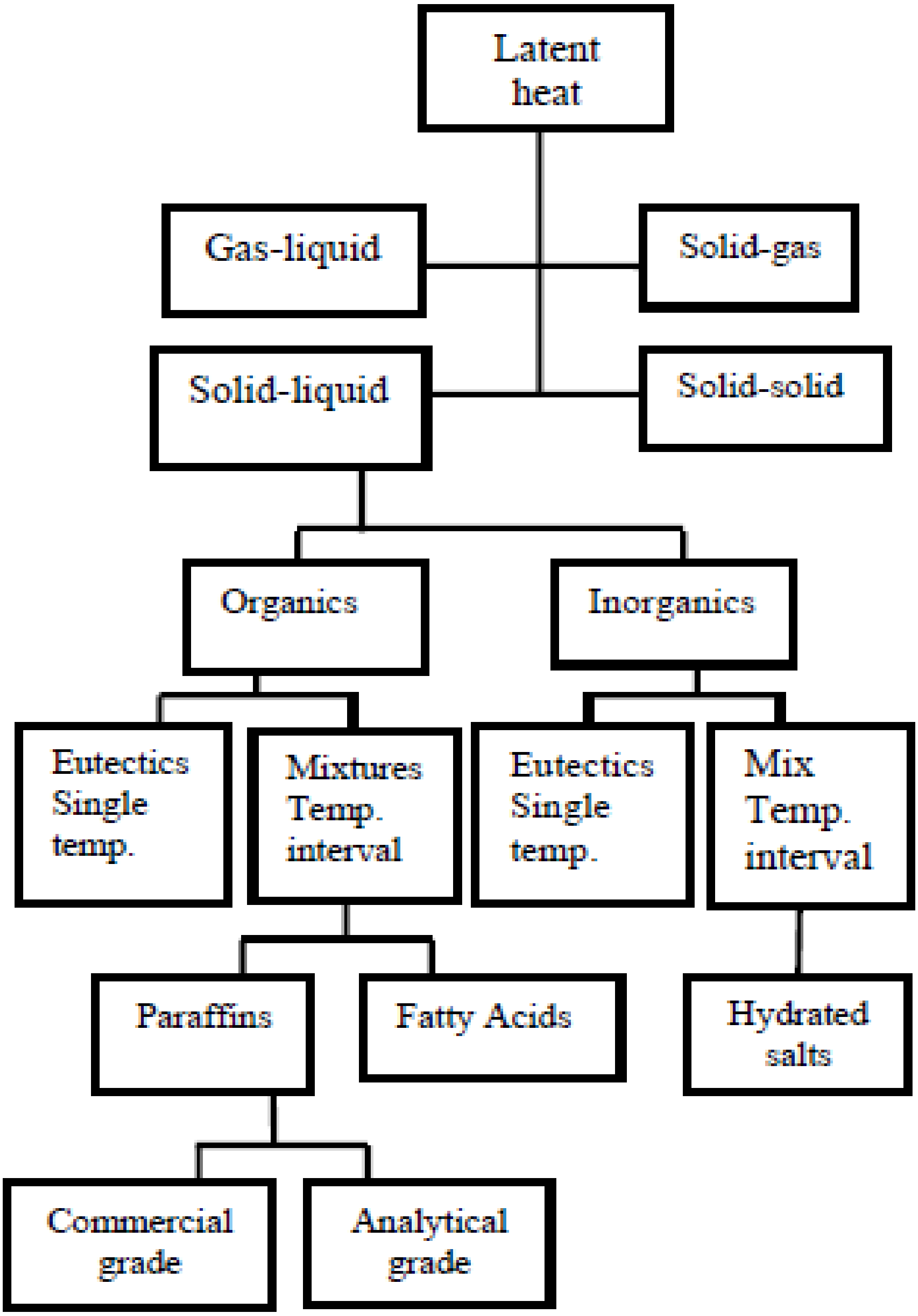


Figure 1. Classification of PCM

PCMs can broadly be arranged into three categories:

2.2.1.1 - ORGANIC PCMS:

Paraffin (C_nH_{2n+2}) and fatty acids ($CH_3(CH_2)_{2n}COOH$)

Organic Thermal Salt can be Aliphatic or Other Organics.

Organic materials used as PCMs tend to be polymers with long chain molecules composed primarily of carbon and hydrogen. They tend to exhibit high orders of crystallinity when freezing and mostly change phase above 0°C (32°F). Examples of materials used as positive temperature organic PCMs include waxes, oils, fatty acids and polyglycols.

- **Advantages**
    1. **Freeze without much super cooling.**
    2. **Ability to melt congruently.**
    3. **Self nucleating properties.**
    4. **Compatibility with conventional material of construction.**
    5. **No segregation.**
    6. **Chemically stable.**
    7. **High heat of fusion.**
    8. **Safe and non-reactive.**
    9. **Recyclable.**
- **Disadvantages**
    1. **Low thermal conductivity in their solid state. High heat transfer rates are required during the freezing cycle.**
    2. **Volumetric latent heat storage capacity is low.**
    3. **Flammable. This can be easily alleviated by a proper container.**
    4. **To obtain reliable phase change points, most manufacturers use technical grade paraffins which are essentially paraffin mixture(s) and are completely refined of oil, resulting in high costs.**

2.2.1.2 - INORGANIC PCMS:

Salt hydrates (M_nH_2O)

Inorganic Thermal Salts are generally Hydrated Salt based materials. Academicians are likely to misguide you into using pure hydrated salts like Sodium Sulphate Decahydrate and so on. Hydrated salts have a number of hydrates and an anhydrous form leading to stratification of material and loss of Latent Heat recovery with time. Hydrated salts also have a sub-cooling tendency. Old generation Thermal Salt manufacturers managed to add performance-enhancing agents. These additives do help in delaying the degradation of the thermal salt for say 100 cycles or thereabout. However, they do not address the basic reasons due to which sub-cooling and degradation happens. Earlier researchers emphasized that it is beneficial to use impure grades of base material as it

promotes the nucleation and prevents sub-cooling. However, impurities also promoted nucleation of undesirable hydrates leading to stratification. Experts on crystallography have managed to identify the "Preferred Crystal Nucleation" method. It consists of a "Cold Finger" that nucleates and promotes the growth of desired crystals and "Detoxification" or "Selective Elimination" whereby any impurity that promotes the growth of undesirable crystals is removed. The current methods of Thermal Salt manufacturing are like the new generation "Combination Drugs".

Salt hydrates are specific salts that are able to incorporate water of crystallization during their freezing process and tend to change phase above 0°C (32°F).

- **Advantages**
  1. **High volumetric latent heat storage capacity.**
  2. **Availability and low cost.**
  3. **Sharp melting point.**
  4. **High thermal conductivity.**
  5. **High heat of fusion.**
  6. **Non-flammable.**
- **Disadvantages**
  7. **Change of volume is very high.**
  8. **Super cooling is major problem in solid–liquid transition.**
  9. **Nucleating agents are needed and they often become inoperative after repeated cycling.**

2.2.1.3 - EUTECTICS **Organic-organic, organic-inorganic, inorganic-inorganic compounds**

Eutectics tend to be solutions of salts in water that have a phase change temperature below 0°C (32°F).

- **Advantages**

  10. **Eutectics have sharp melting point similar to pure substance.**
  11. **Volumetric storage density is slightly above organic compounds.**

- **Disadvantages**
  1. **Only limited data is available on thermo-physical properties as the use of these materials are very new to thermal storage application**

2.2.2. Applications

1) Flat ICE Containers:

These containers are constructed of blow Molded HDPE and can be filled with positive or negative temperature PCMs, although high temperature PCMs may be unsuitable due to softening of the plastic.

Each container holds approx 3 litres of PCM and due to their design they can be stacked on top of each other to achieve a large bulk volume of PCM for, e.g., building temperature control applications. When stacked there is a small gap between each container, allowing either air or water to flow easily over the containers while providing a large PCM surface area for heat transfer.

2) Tube ICE:

These containers operate on a similar principle to the Flat ICE containers, and are supplied as fully sealed PCM-filled HDPE tubes. The tubular design enables them to be stacked effectively in both rectangular and cylindrical tanks with minimal void space.

Once installed, a series of ridges around the circumference of the tube mean that air or water can pass freely between the containers allowing excellent heat exchange properties.

3) Ball ICE:

This technology is only available for use with our positive temperature organic range of PCMs, and involves the PCM being directly incorporated into a plastic or rubber matrix. This is then moulded to produce standard sized balls, although any shape or size can be

moulded if required. This concept is ideal for heat storage applications such as solar, waste heat, hot water, and domestic/commercial heating tanks.

4) Eutectic Plates :

This catalogue acts as an introductory guide to the methods of encapsulation available for our sub-zero eutectic PCMs, and their typical modes of application and uses.

Our standard Eutectic plates are 500mm x 250mm x 32mm and Ice Packs are

190mm x 120 mm x 25 mm can be filled any of our Eutectic solution but any

other dimensional shape, fitting and temperature

requirements can be supplied as a custom-made

product together with full application support.

Please consult our technical team for any

special application you may have in mind.

5) PCM Pouches:

The bulk of the range of our PCMs can be supplied prefilled in a wide variety of flexible metallic or

non-metallic pouches, available in a number of

different sizes for use in temperature critical

transport applications. Alternatively, we can fill

majority of our Plus ICE range PCM solution in

our customer's own pouches as well as develop custom-made sizes using special materials for a variety of temperature range applications.

6) Transport Eutectic Plates :

A wide range of metallic eutectic plates manufactured

by FIC (Italy) are available in a number of different sizes,

and filled with several standard eutectic solutions to

cover a multitude of conventional applications and

operational temperature ranges. However, if any special

application is required, we can fill them with any of our Plus ICE PCM solutions to suit the application. Both standard carbon and stainless steel with or without a cooling coil fitted versions can be used with or without a refrigeration circuit.

7) Passive Cooling:

A passive cooling energy storage application designed to work the natural difference between the cooler night and warmer day time ambient temperatures and by storing the cold energy over-night, the daily heat gains both internally and externally can be handled without any mechanical refrigeration, thereby providing maintenance free passive cooling system.

8) EcoPacBOX:

Another passive cooling application, this time targeted at maintaining operational temperatures in temperature sensitive areas such as computer rooms, telecoms shelters, or any enclosed space containing electrical equipment capable of generating heat. Many such pieces of equipment are specified not to be used in ambient temperatures greater than 45 °C (113 °F). The EcoPacBOX design complements, or eliminates altogether, the need for mechanical cooling in such spaces.

Cold Storage, Shipping and Sundry Application:

Several Types of Packing can be custom made for cold storage and shipping application. Insulated Containers having back up of PCM of appropriate temperature (like -40^{o}C or say +18^{o}C) can be offered. As a demonstration, we have shown below a small size "PCM backed Insulated Container". It has four PCM filled profiles inserted in a special high-class insulated box. The box was kept for 30 days at 18^{o}C by filling it with appropriate PCM. Containers of any size and shape can be tailor made.

2.2.3 Selection Criteria

we select the suitable phase change material to our application according to the following:

- **Thermodynamic properties:**

  1. Melting temperature in the desired operating temperature range
  2. High latent heat of fusion per unit volume
  3. High specific heat, high density and high thermal conductivity
  4. Small volume changes on phase transformation and small vapor pressure at operating temperatures to reduce the containment problem
  5. Congruent melting

- **Kinetic properties**

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

- **Chemical properties**

  1. Chemical stability.
  2. Complete reversible freeze/melt cycle.

3. **No degradation after a large number of freeze/melt cycle.**
4. **Non-corrosiveness, non-toxic, non-flammable and non-explosive materials.**

- **Economic properties**

1. **Low cost.**
2. **Availability.**

2.3 PCM for Domestic solar Water Heating

Phase change materials can be introduced in the solar heating system as a latent heat storage system in two different ways :

1) it can be used as a shell for solar collector tubes so it enhance energy absorbed from sun during day time.

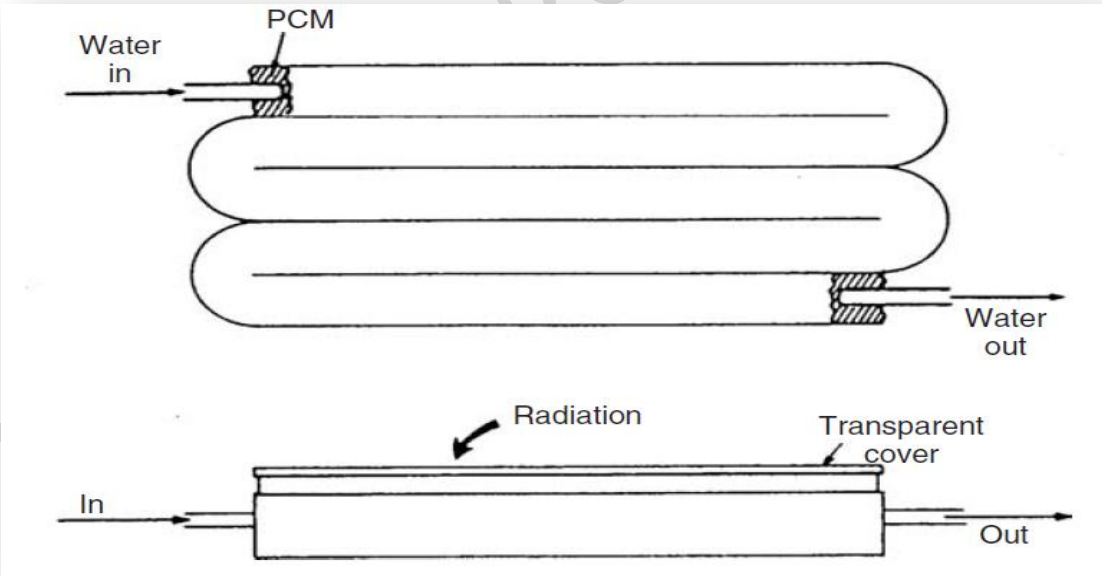


Figure 2.2

2) the other method is to put the phase change material inside storage tank and this method requires choosing the suitable technique of PCM container.

Technology, development and encapsulation

The most commonly used PCMs are salt hydrates, fatty acids and esters, and various paraffins (such as octadecane). Recently also ionic liquids were investigated as novel PCMs.

As most of the organic solutions are water-free, they can be exposed to air, but all salt based PCM solutions must be encapsulated to prevent water evaporation or uptake. Both types offer certain advantages and disadvantages and if they are correctly applied some of the disadvantages become advantages for certain applications.

They have been used since the late 1800s as a medium for the thermal storage applications. They have been used in such diverse applications as refrigerated transportation for rail and road applications and their physical properties are, therefore, well known.

Since PCMs transform between solid–liquid in thermal cycling, encapsulation naturally becomes the obvious storage choice.

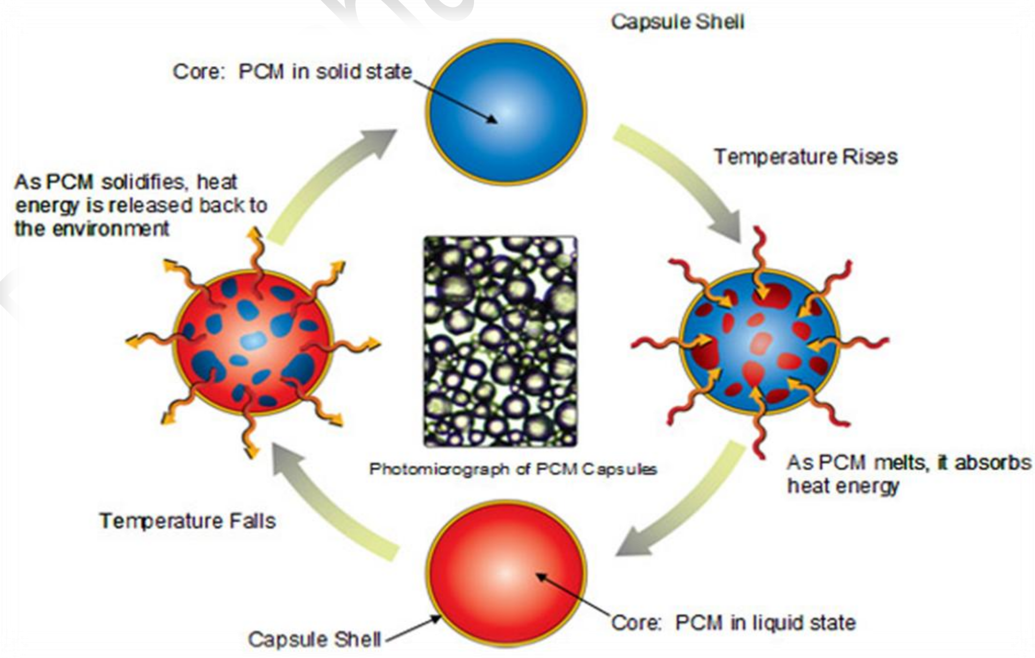
Encapsulation of PCMs

- Macro-encapsulation: Early development of macro-encapsulation with large volume containment failed due to the poor thermal conductivity of most PCMs. PCMs tend to solidify at the edges of the containers preventing effective heat transfer.
- Micro-encapsulation: Micro-encapsulation on the other hand showed no such problem. It allows the PCMs to be incorporated into construction materials, such as concrete, easily and economically. Micro-encapsulated PCMs also provide a portable heat storage system. By coating a microscopic sized PCM with a protective coating, the particles can be suspended within a continuous phase such as water. This system can be considered as phase change slurry (PCS).
- Molecular-encapsulation is another technology, developed by Dupont de Nemours that allows a very high concentration of PCM within a polymer compound. It allows storage capacity up to 515 kJ/m^2 for a 5 mm board (103 MJ/m^3). Molecular-encapsulation allows drilling and cutting through the material without any PCM leakage.

As phase change materials perform best in small containers, therefore they are usually divided in cells. The cells are shallow to reduce static head – based on the principle of shallow container geometry. The packaging material should conduct heat well; and it should be durable enough to withstand frequent changes in the storage material's volume as phase changes occur. It should also restrict the passage of water through the walls, so the materials will not dry out (or water-out, if the material is hygroscopic). Packaging must also resist leakage and corrosion. Common packaging materials showing chemical compatibility with room temperature PCMs include stainless steel, polypropylene and polyolefin.

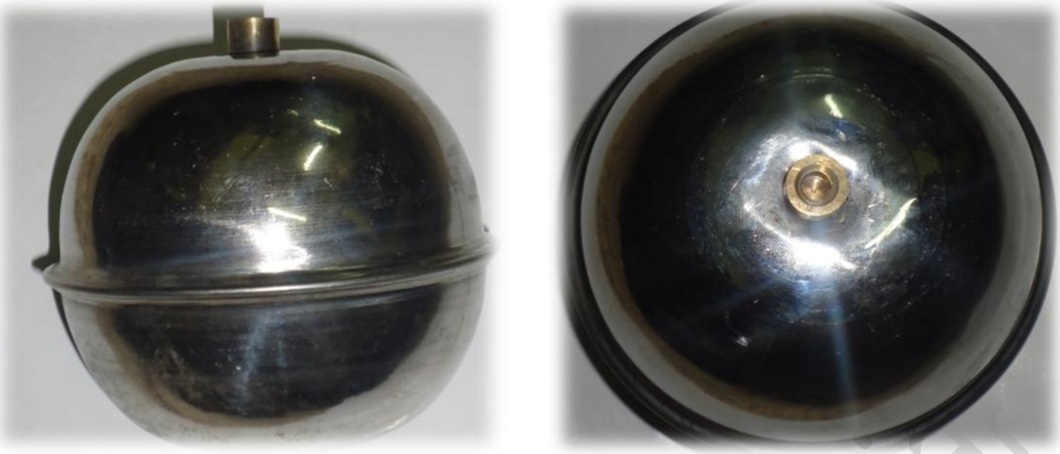
2.3.1 Operating Theory and the Reason of Using Paraffin Wax

Encapsulated phase change materials (PCMs) consist of an encapsulated substance with a high heat of fusion. The phase change material absorbs and releases thermal energy in order to maintain a regulated temperature within a product such as textiles, building materials, packaging, and electronics. The capsule wall or shell provides a microscopic container for the PCM. Even when the core is in the liquid state, the capsules still act as a solid – keeping the PCM from “melting away.”



<u>Fig 2.3</u> processes of melting and freezing inside PCM capsule

We use a metallic sphere encapsulated PCM as shown below



<u>Fig 2.4</u> PCM stainless steel capsule that we used

In our project we use paraffin wax as the phase change material.

<u>Fig 2.5</u> this is paraffin wax in solid state

We choose paraffin wax due to the following reasons:

1. **Its Melting temperature is at 54^{o}C, so it is in the desired operating temperature range**

2. **High latent heat of fusion per unit mass. It is about 266 KJ/kg.**
3. **Small volume changes on phase transformation and small vapor pressure at operating temperatures to reduce the containment problem**
4. **Congruent melting**
5. **High nucleation rate to avoid super cooling of the liquid phase.**
6. **High rate of crystal growth, so that the system can meet demands of heat recovery from the storage system.**
7. **Chemical stability.**
8. **Complete reversible freeze/melt cycle.**
9. **No degradation after a large number of freeze/melt cycle.**
10. **Non-corrosiveness, non-toxic, non-flammable and non-explosive materials.**
11. **Low cost.**
12. **Availability**

2.3.2 Advantage of Using Paraffin Wax for solar water heating Applications:

When we use paraffin wax for solar water heating application, we use it inside storage tank. Now it acts as a latent heat storage system storing possible heat during day and gives it to surrounding water by conduction and convection during all-night. It occupy a small volume inside collector but its thermal storage capacity is large so it enhances the storing performance and hence it improve the efficiency of whole solar water heating system.

2.3.3 Paraffin Wax Properties

Latent Heat of Fusion (h_{fg})……….= 266 kJ/kg

Melting Temperature (T_m)……….= 54 °C

Solid Phase Density (ρ_s)……............ = 810 kg/m^3

Liquid Phase Density (ρ_L)…………= 780 kg/m^3

Thermal Conductivity……………= 0.21 W/m K

Solid Phase Specific Heat (Cp)…...= 2.9 kJ/kg K

Liquid Phase Specific Heat (Cp)…= 2.13 kJ/kg K