

PHASE CHANGE MATERIALS: CHARACTERISTICS AND ENCAPSULATION

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Abstract- Over the past few decades researchers and analysts are searching for new technologies that will cut down the consumption of conventional fuels to decrease the negative impacts on climate and environment. Thermal Energy storage (TES) through the usage of Phase Change Materials (PCM) is one those approaches through which alternative energy can be generated; which not only reduces the variance between supply and demand but also increases the stability of energy supply in addition to energy conservation. We will call PCM only those materials which possess certain characteristics like- high thermal conductivity, large latent heat and a few others. The realistic applications of PCM and their financial feasibilities will be described. Though the durability of PCMs over numerous cycles can be questionable, the encapsulation significantly increases their efficiency and resilience. Successful and efficient storage of solar energy through PCM can be highly beneficial to take the implementation of renewable energy to the next level.

Keywords: TES, PCM, Encapsulation, Energy storage, Solar energy.

1. INTRODUCTION

Energy has been the main driver behind the growth and development of modern civilization. World economic development is more dependent than ever on energy. However, the field of energy faces major challenges like improving efficiency, reducing of fossil fuel consumption and CO₂ emissions and developing alternative renewable energy sources. Over the past decades researchers all over the world are searching for new technologies which will cut down the usage of fossil fuels and eventually, decrease the negative impact on climate and environment through energy generation. Energy storage is one those suitable methods through which alternative energy can be produced. Energy storage does not only reduce the variance between supply and demand but also increases the stability and quality of energy supply in addition to conserving energy.

Thermal Energy Storage (TES) is one of the most commonly used methods of energy storage. TES can be classified into two main categories- i. Sensible heat storage and ii. Latent heat storage. Increase of energy from heating of a substance is shown in the following figure.

The process of figure-1 includes sensible heating, in regions A-B, C-D, E-F and G-H, and also latent heating- in B-C, D-E and F-G regions. Total amount of energy

stored per unit weight is equal to the summation of integration for specific heat of material in phase transition with temperature difference. For sensible heat transfer larger amount of medium is required storing same amount of energy than that of latent heat transfer. Due to small latent heat in solid-solid transition and the requirement of large volume for liquid-gas transformation- these two options are not technically viable. [1] Furthermore, as energy storage in the case of solid-liquid transformation is of higher density and operates at a constant temperature as PCM we will only mean energy storage through this transformation.

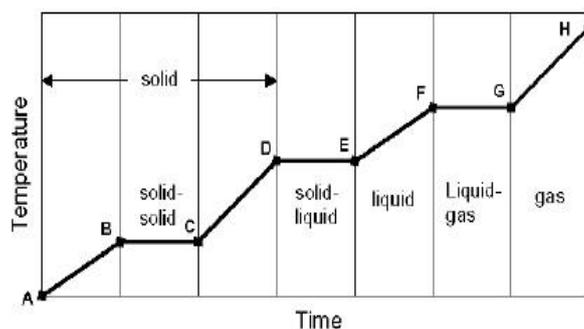


Figure 1: temperature v time diagram for heating of a

substance [2]

PCM mainly depends on the latent heat storage, while storage through sensible heat relies on change in temperature of materials. Thermal energy storage through PCM is capable of storing and releasing of energy in large quantity. The holding and releasing of energy depends on the change in phase of the materials. Practical experiments have shown that a major reduction in storage volume can be attained through PCM compared to Sensible heat storage.

Hasnain had shown very clearly how latent heat storage is much more beneficial to sensible heat storage.

Table 1: Comparison between different methods of heat storage [3]

Property	Rock	Water	Organic PCM	Inorganic PCM
Density, kg/m ³	2240	1000	800	1600
Specific heat, kJ/kg	1.0	4.2	2.0	2.0
Latent heat, kJ/kg	–	–	190	230
Latent heat, kJ/m ³	–	–	152	368
Storage mass for 10 ⁶ J, kg	67,000	16,000	5300	4350
Storage volume for 10 ⁶ J, m ³	30	16	6.6	2.7
Relative storage mass	15	4	1.25	1.0
Relative storage volume	11	6	2.5	1.0

2. PHANGE CHANGE MATERIALS

PCMs are latent heat thermal energy storage materials which use their chemical bonds for the storage and releasing of energy. When PCMs reach the temperature at which they melt, they absorb large amount of energy without getting heated. PCMs solidify and releases energy when the surrounding temperature drops.

Though in a sense every material is a phase change material, in energy storage we call PCM only those materials which posses certain characteristics for energy storage. Phase change materials for energy storage should have a high thermal conductivity and large latent heat. Additionally, the melting point of the substances should lie within realistic range of application; materials should be chemically stable and should melt congruently with least supercooling. Chemically, the materials also must be non-toxic and non- corrosive. Financially, PCMs should be available and very cost effective. According to the researches done over the last few decades- types of paraffin, salt hydrants, fatty acids and sugar alcohols are

suitable for usage as Phase Change Materials though none of those materials posses all the properties of an ideal PCM. Below is a list of PCM manufacturers.

Table 2: PCM manufacturers and number of PCMs [4]

Serial	Manufacturer	Temperature range	Nos. of listed PCM
1	EPS	-114 ⁰ C to 164 ⁰ C	61
2	Rubitherm	-3 ⁰ C to 100 ⁰ C	29
3	Cristopia	-33 ⁰ C to 27 ⁰ C	12
4	TEAP	-50 ⁰ C to 78 ⁰ C	22
5	Doerken	-22 ⁰ C to 28 ⁰ C	2
6	Climator	-18 ⁰ C to 70 ⁰ C	9

3. TYPES OF PCM

PCMs are generally categorized into two groups: (a) Organics and (b) Inorganics. [1] Another group of PCMs is the 'Eutectics'. But they are not considered as a main group for two reasons- very few PCMs are truly Eutectics' & most of those are modified before any practical application [5]. Both of the major groups have their merits and demerits as shown below.

Table 3: Comparison of Organic and Inorganic PCMs [6]

	Merits	Demerits
Organic	Chemically stable	Costlier
	Non-corrosive	Wide melting range
	No supercooling	Lower latent heat capacity
		Lower thermal conductivity
Inorganic	Less expensive	Supercooling
	Higher latent heat per unit volume	Corrosive
	Higher thermal conductivity	Less stability
	Non-flammable	

3.1 Organic Materials

Organic materials can be further divided into paraffins and non- paraffins. [7].

Paraffins: Chemically, the crystallization of the paraffins, (CH₃) - releases a good amount of latent heat. Due to the high cost of paraffins only technical class paraffins are used as PCMs. Paraffins are generally stable below 500⁰C and do not change significant volume change on melting and also possess a low vapor pressure in melt condition. The main reason behind paraffin's qualification as an energy storage material is their accessibility in wide range of temperatures. They are consistent, safe, knowable and generally, non-corrosive.

Group I and II materials are very good to be used as PCMs while group III substances are not as promising as PCMs [7]. Commercial paraffins are low cost with moderate thermal storage density and wide melting points but their main problem is very low thermal conductivity. On the other hand, pure paraffins are highly costly which limits their application. That's is why metallic fins are used to increase the thermal conductivity of the commercial paraffin and nucleating agent is used to suppress the supercooling. Below is a list of fusions of paraffins usable as PCM.

Table 4: List of Paraffins as PCM [1]

Compound	Melting point (K)	Heat of fusion (kJ/kg)
Paraffin C ₁₄	277.7	165
Paraffin C ₁₅ - C ₁₆	281.2	153
Paraffin C ₁₆ - C ₁₈	294.2	152
Paraffin C ₁₃ - C ₂₄	296.2	189
Paraffin C ₁₆ - C ₂₈	316.2	189
Paraffin C ₁₈	301.2	244
Paraffin C ₂₀ - C ₃₃	322.2	189
Paraffin C ₂₂ - C ₄₅	300.7	23.5
Paraffin C ₂₃ - C ₅₀	340.4	189
Paraffin wax	337.2	173.6

Non-Paraffins: There are numerous materials for phase change energy storage in this category. In fact this the largest category for PCMs. Buddhi and Sawhney [9] have conducted vast analyses on organic materials and showed that there are quite a lot of esters, fatty acids, glycols and alcohols which can serve for latent heat energy storage. Fatty acids like capric acid, lauric acid, palmitic acids have melting points between 30-65C, having latent heat between 150-180 KJ/KG. These acids also show good melting and freezing behaviors with no supercooling. Fatty acids formulation of CH₃(CH₂)_{2n}.COOH makes them qualified as good quality PCMs. The main problems associated with the fatty acids are – they are 2-3 times costlier and moderately corrosive. The property of mildly corrosiveness when used as PCM is another disadvantage of the fatty acids. The general tendencies of fatty acids are shown in the table.

Table 5: Melting point and latent heat of fusion of fatty acids [7]

Material	Formula	Melting point (°C)	Latent heat (kJ/kg)	Group
Acetic acid	CH ₃ COOH	16.7	184	I
Polyethylene glycol 600	H(OC ₂ H ₂) _n O H	20–25	146	I

Capric acid	CH ₃ (CH ₂) ₈ C OOH	36	152	–
Eladic acid	C ₈ H ₇ C ₉ H ₁₆₃ C OOH	47	218	I
Lauric acid	CH ₃ (CH ₂) ₁₀₃ C OOH	49	178	II
Pentadecanoic acid	CH ₃ (CH ₂) ₁₃₃ C OOH	52.5	178	–
Tristearin	(C ₁₇ H ₃₅ COO) C ₃ H ₅	56	191	I
Myristic acid	CH ₃ (CH ₂) ₁₂₃ C OOH	58	199	I
Palmitic acid	CH ₃ (CH ₂) ₁₄₃ C OOH	55	163	I
Stearic acid	CH ₃ (CH ₂) ₁₆₃ C OOH	69.4	199	I
Acetamide	CH ₃ CONH ₂	81	241	I
Methyl fumarate	(CHCO ₂ NH ₃) ₂	102	242	I

3.2 Inorganic Materials

Inorganic PCMs are also divided into two classes- salt hydrates and metallics.

Salt hydrates are highly attractive materials for phase change energy storage thanks to their cost effectiveness, higher thermal conductivity and small volumetric changes for storage. For example, Glauber salt (Na₂SO₄.6H₂O); which has melting point of 32.4C and a very high latent heat of 254KJ/KG. But the phase segregation and supercooling tends to limit its practical application. However, some thickening substances and a nucleate agent can be used to overcome the problem of the phase segregation and sub-cooling respectively. GE Co., NY [11] suggested a rolling cylinder heat storage system which includes a cylindrical vessel mounted horizontally with two sets of rollers. Generally, other salt hydrates also show the same problems more or less. Despite having the above limitations hydrated salts are counted as the most important type of PCMs as their advantages surpass their drawbacks.

Low melting metals were also considered for phase change energy storage because of their high thermal conductivity and their higher heat of fusion per unit volume. But their weight and some other technical problems made them unpopular among the scientists.

4. PROBLEMS

The main problem associated with the PCMs is the number of cycles they can withstand without decreasing any of their properties. There are two reasons behind the lack of long term efficiency of the materials- a) poor stability of the materials characteristics and b) reaction between the materials and the containers. The containers must be developed in such a way that the PCM must be able to go repetitive cycles of cooling and heating

without causing any corrosion. Thermal cycling tests are carried out to ensure that the materials under test do not deviate from their PCM properties after long usage.

NaCl was used by Kimura & Kai [12] to improve the stability of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Their experiment was very successful and endured more than a thousand cycles. Later Gibbs and Hasnain [13] proved that paraffins also have very good thermal stability under numerous cycles. The reason behind the popularity of salt hydrates as PCM also is this stability test result which showed a little or no corrosion. [14, 15]. The storage density of the PCMs also decreases with cycling. Density is highly important for the PCM as the energy storage is directly linked to the per unit volume and as salt hydrates are possess a higher density than the paraffins they are more used as PCM. The table below was reported by Lane to show the thermophysical properties of a number of PCMs: [16].

Table 6: Thermophysical properties of PCMs

Compound	Melting temp. ($^{\circ}\text{C}$)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m^3)
Inorganics				
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	117	168.6	0.570(liquid, 120°C)	1450(liquid, 120°C)
			0.694(solid, 90°C)	1569(solid, 20°C)
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	89	162.8	0.490(liquid, 95°C)	1550(liquid, 94°C)
			0.611(solid, 37°C)	1636(solid, 25°C)
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	48	265.7	0.653(liquid, 85.7°C)	1937(liquid, 84°C)
			1.225(solid, 23°C)	2070(solid, 24°C)
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	29	190.8	0.540(liquid, 38.7°C)	1562(liquid, 32°C)
			0.1.088(solid, 23°C)	1802(solid, 24°C)
Organics				
Paraffin wax	64	173.6	0.167(liquid, 63.5°C)	790(liquid, 65°C)
			0.346(solid, 33.6°C)	916 (solid, 24°C)
Polyglycol E600	22	127.2	0.189(liquid, 38.6°C)	1126(liquid, 25°C)
			–	1232(solid, 4°C)

Fatty Acids				
Palmitic acid	64	185.4	0.162(liquid, 68.4°C)	850(liquid, 65°C)
			–	989(solid, 24°C)
Capric acid	32	152.7	0.153(liquid, 38.5°C)	878(liquid, 45°C)
			–	1004(solid, 24°C)
Caprylic acid	16	148.5	0.149(liquid, 38.6°C)	901(liquid, 30°C)
			–	981(solid, 13°C)
Aromatics				
Naphthalene	80	147.7	0.132(liquid, 83.8°C)	976(liquid, 84°C)
			0.341(solid, 49.9°C)	1145(solid, 20°C)

Another vital problem for the PCMs is supercooling. The presence of liquid below the freezing temperature during freezing is called supercooling. Supercooling decreases the temperature difference between PCM and the fluid for transfer, which lengthens the time for charging and discharging. [17] To minimize these problems scientists have hydrated salts in direct contact heat transfer between an immiscible heat transfer fluid and the hydrated salt solution. The agitation caused by the heat transfer fluid has decreased the supercooling and prevented phase segregation.

One more major setback of the PCMs is their low thermal conductivity. That is why enhancement of heat transfer is required for most of the phase change materials. Various methods have been applied to increase the conductivity of the materials used for latent heat thermal storage. Metallic fillers, finned tubes, matrix metallic structures are used to enhance the conductivity of PCMs.

5. ENCAPSULATION

Encapsulation has become really important for PCMs now-a-days for their efficiency. Encapsulation commonly refers to the arrangement of a layer for the material which detaches the PCM from the heat transfer fluid and makes them more compatible for usage. Encapsulation has proved to increase the heat transfer area for most of the PCMs. Lessening the PCMs reaction tendency to outer environment including the container has also been a great advantage of using encapsulations. Lane [18, 19] has experimented microcapsulation on $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in plastic thin containers and showed that better heat transfer is possible using air as the medium.

Finally, after a vast number of experiments he lastly decided to use $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ encapsulated in plastic pipes. The technical and financial practicability was of encapsulation was thoroughly examined by him and considered encapsulated PCMs for solar heating in residences.

Stark infiltrated paraffin and polyethylene wax into extruded films of polymer by a solvent exchange technique to generate microcomposites with PCM. The yielded microcomposites showed outstanding chemical and mechanical stability under cyclic freeze-thaw conditions. [20]

Ammonium Nitrate and Ammonium alum form a eutectic PCM which melts at 53°C and –crystallizes at 48°C . Its enthalpy was found to be KJ/Kg in the temperature range of $25\text{-}67^\circ\text{C}$ which is 1.5 times greater than water and after several cycles its stability as found to be deviate from the standard behavior; and phase segregation was occurring. But Goswami and Jotshi [21] showed that adding 5% attapulgitic clay with it and encapsulating the eutectic in HDPE (High Density Polyethylene) hollow balls prevented not only the phase segregation but also its stability up to 1100 heating and cooling cycles. Nevertheless, the potential use of microencapsulation of PCMs in various thermal control applications is limited due to their relatively higher cost. [22].

Detailed mathematical experiments of many energy storage systems with encapsulated PCMs will be used in recent future to increase energy storage density and heat transfer performance. [23, 24]. Existing simplified models of PCM based systems with encapsulation may prove to be most effective for energy storage. [25]. Encapsulation also makes PCMs usable for building industries.

6. APPLICATION

Lots of attempts have been taken to store solar energy into PCMs in order to use the energy, stored in daytime, in the nights. As most of the PCMs have low thermal conductivity they must be encapsulated in such a way that significant reduction of the heat transfer rate can be avoided. Chaurashia [26] suggested that high thermal conductive materials to be used with PCMs to improve the conductivity of the whole process. Furthermore, experiments showed that several PCMs of different melting temperatures used in a large thin flat container improved the performance of the energy storage system by far. Results also, showed that latent heat storage system produces more hot water than the sensible heat storage system.

One of the most prospective applications of PCMs is in the residential buildings. Though this application was discovered later but it accelerated over the past several years. Phase change materials energy storage capacity is very helpful for effective use of solar energy in buildings. It is examined that paraffin mingled with suitable hydrocarbons can obtain the required melting point for these applications [27].

More recently, PCMs are being seen as replacement

for the conventional power supply for the satellite system [28]. In the central of the solar power system there are metal cells which contain PCMs. These PCMs are liquid in high temperature and releases heat in the cold, which can be used later for electricity using thermoelectric methods.

7. CONCLUSION

Energy storage method using phase change materials has a lot of advantages because of the less mass and volume of the system. Moreover, in this system energy is stored in a steady temperature and loss of energy is much less than the conventional systems. Energy storage through PCM is and will be very beneficial to energy conservation as well as to the human civilization. Till now Phase Change Materials are only used solar water-heating, solar air heating, space heating and cooling applications and it is certain that a lot more usage of the PCMs are yet to be discovered.

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