A Review on the Utilization of Phase Change Materials for Space Cooling Purposes

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Abstract. Thermal energy storage systems have been investigated for the last decades, even though the information is quantitatively enormous with a few application works. In this study, a review has been carried out for the applications of phase change materials in the cooling of buildings, where these materials have tendency to gain extra heat (latent heat) during solid–liquid phase change. The study presents significant information regarding the use of phase change materials for cooling with many considerations like: climate conditions, types of phase change materials and their thermo-physical properties. The resultant studies show that the integration of phase change material in the building have a good potential for reducing energy demand for cooling, further investigations are needed to really assess their benefits.

Keywords: Thermal energy storage, phase change materials, cooling, passive, buildings.

1. Introduction

It has been revealed that the benefits of energy conservation can be achieved through the incorporation of thermal energy storage (TES) in the field of construction and industry [1]. The use of TES bridges the gap between energy demand and supply when applied to active and passive systems by utilizing the waste energy, using techniques for adjusting peak load and consuming thermal energy in a reasonable manner [2]. The application of TES in a system ensures the enhancement in total performance and more consistency besides improving the finances through the reduction of operating cost. TES is also eco-friendly as it releases small amount of carbon dioxide gas into the atmosphere [3]. Storage heat can be achieved in an active or passive way with respect to the application used [4]. The natural resources of heating are developed by the passive TES systems for regulating the temperature of a building consequently reducing the dependence on electrical equipment [5]. The last two decades have witnessed considerable research on TES especially on the phase change materials (PCMs). There is a vast content available on this subject and its handling is very critical. The application of energy storage is a global interest since it has concerned with the worldwide issues of energy conservation, as well as optimum use of the resources and renewable energies [6]. By applying suitable phase change materials (PCMs) to the walls, ceiling and floors of buildings, the desired temperature interval is maintained for a longer period of. Due to its capability of storing significant thermal energy within a small volume, using a PCM as a latent heat storage material, has gained increasing attention recently, and this making it one of the most promising technologies for improving energy efficient buildings. The heat could be absorbed or released when the PCMs changes from one phase to another. The main phase change of interest is the solid-liquid phase change than other phase change types [1, 2]. Many previous studies mentioned the PCMs as materials and focused upon the corresponding analysis related to thermo-chemical process. They have not introduced the PCMs in the
perspective of which material is useful for certain cooling application and the limitation depending on their properties. Furthermore, the majority of sources present the idea of using PCMs as heat storage material for heating purposes.

2. Thermal energy storage (TES)
Substances used for TES can be classified into many categories. A useful classification of these materials is shown in Figure 1. Abhat [7], Lane [8, 9] and Dincer and Rosen [10] can be referred to comprehend the phase change materials. These references provide an absolute analysis of various phase changing materials along with a detailed review of their categorization, properties, advantages and disadvantages. These references also highlight the strategies for evaluating how these materials react during phase changing.

![Figure 1. Classification of energy storage materials [7]](image)

Following are the features of the PCMs that are imperative for a system [11]:
1. Heat Storage: It is essential for the PCM to possess considerable latent heat of fusion. An adequate range of sensible energy must also be present in the PCM. This implies that storage energy during the melting phase can be enhanced by the higher density of the material.
2. Melting Point: The range of melting (or solidifying) point of the PCM must be small however; it must not be too small. It must be reasonable. Water is the perfect example of reasonable melting point. Water is characterized by distinct freezing temperature of 0°C. However, most PCMs do not have fixed melting points and their melting points may vary slightly from the definite melting point. This property is known as hysteresis.
3. Super Cooling: The property of super cooling means that the physical state of the liquid PCM is retained even after it reaches the melting point and is cooled down. This means that the PCM has an alternative melting point. Usually, eutectic solutions and salt hydrates show this property.
4. Stability: An ideal PCM is one that remains stable during the melting and freezing processes. During their long term use, PCMs undergo melting and freezing processes numerous times.
Hence, it is imperative for them to show stability since their physical and chemical instability may reduce their potential to store energy.

5. Not Dangerous: PCMs are usually used in household applications like temperature controlling in homes and storage of food, hence, it must be ensured that the used PCMs do not pose any danger to human life.

6. Have a Reasonable Cost: The PCMs may be cheap and expensive. The cheap ones include water and the costly ones include pure linear hydrocarbons. It is important to consider the cost of the PCMs as compared to their offered benefits. If the cost is more as compared to the advantages, then other cost-effective applications must be used with lower amount of PCMs.

3. Classification of phase change materials

Although there is a wide range of PCM materials, they can be classified mainly as paraffin and salt hydrates [12]. Figure 2 shows that both these groups have their distinct range of melting point and latent heat of fusion.

4. Thermo-physical properties of phase change materials

The essential properties of PCMs are shown in Tables 1&2 for both paraffin and salt hydrate, respectively [13-20]. The heat analysis method and appropriate strategies for analysis for an application can be indicated by thermo-physical characteristics. Various tools such as the differential scanning calorimetry (DSC) and differential thermal analysis (DTA) along with some traditional tools may be employed to evaluate these characteristics. Flaherty [16] has presented a reliable research regarding the DSC to comprehend the description of natural waxes and hydrocarbons. Moreover, Giavarini [17] provided a detailed review about the description of petroleum products. Gibbs [18] stated that the producers of the chemical substances are likely to present uncertain property values, therefore, it is recommended to get correct values by making use of DSC. The traditional methods of estimating the PCM property values were highlighted by Yinping [19]. He also highlighted the drawbacks of these traditional approaches.

Figure 2. Classification of PCMs according to the thermal behavior [12]

Table 1. Thermo-physical properties of ParaffinPCMs[13-20]
| Compound                        | Melting temperature (°C) | Heat of fusion (kJ/kg) | Thermal conductivity (W/mK) | Density (kg/m³) |
|--------------------------------|--------------------------|------------------------|-----------------------------|-----------------|
| Paraffin C₁₄                  | 4.5                      | 165                    | n.a.                        | n.a.            |
| Paraffin C₁₅–C₁₆              | 8                        | 153                    | n.a.                        | n.a.            |
| Polyglycol E400               | 8                        | 99.6                   | 0.187 (liquid, 38.6 °C)     | 1125 (liquid, 25 °C) |
|                              |                          |                        | 0.185 (liquid, 69.9 °C)     | 1228 (solid, 3 °C)  |
| Dimethyl-sulfoxide (DMS)      | 16.5                     | 85.7                   | n.a.                        | 1009 (solid and liquid) |
| Paraffin C₁₅–C₁₆              | 20–22                    | 152                    | n.a.                        | n.a.            |
| Polyglycol E600               | 22                       | 127.2                  | 0.189 (liquid, 38.6 °C)     | 1126 (liquid, 25 °C) |
|                              |                          |                        | 0.187 (liquid, 67.0 °C)     | 1232 (solid, 4 °C)  |
| Paraffin C₁₃–C₂₄              | 22–24                    | 189                    | 0.21 (solid)                | 0.760 (liquid, 70 °C) |
|                              |                          |                        |                             | 0.900 (solid, 20 °C)  |
| 1-Dodecanol                   | 26                       | 200                    | n.a.                        | n.a.            |
| Paraffin C₁₈                  | 28                       | 244                    | 0.148 (liquid, 40 °C)       | 0.774 (liquid, 70 °C) |
|                              |                          |                        | 0.15 (solid)                | 0.814 (solid, 20 °C)  |
| 1-Tetradecanol                | 38                       | 205                    | 0.21 (solid)                | 0.765 (liquid, 70 °C) |
| Paraffin C₁₆–C₂₃              | 42–44                    | 189                    | 0.21 (solid)                | 0.910 (solid, 20 °C)  |
| Paraffin C₂₀–C₃₃              | 48–50                    | 189                    | 0.21 (solid)                | 0.769 (liquid, 70 °C) |
| Paraffin C₂₂–C₄₅              | 58–60                    | 189                    | 0.21 (solid)                | 0.912 (solid, 20 °C)  |
|                              |                          |                        |                             | 0.795 (liquid, 70 °C) |
| 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) |
|                              |                          |                        | 0.339 (solid, 45.7 °C)      |                 |
| Polyglycol E6000              | 66                       | 190.0                  | n.a.                        | 1085 (liquid, 70 °C) |
| Paraffin C₂₃–C₅₀              | 66–68                    | 189                    | 0.21 (solid)                | 1212 (solid, 25 °C)  |
| Biphenyl                       | 71                       | 119.2                  | n.a.                        | 830 (liquid, 70 °C)  |
|                              |                          |                        |                             | 0.930 (solid, 20 °C)  |
| Propionamide                  | 79                       | 168.2                  | n.a.                        | 991 (liquid, 73 °C)  |
|                              |                          |                        |                             | 1166 (solid, 24 °C)  |
| Naphthalene                   | 80                       | 147.7                  | 0.132 (liquid, 83.8 °C)     | 976 (liquid, 84 °C)  |
|                              |                          |                        | 0.341 (solid, 49.9 °C)      | 1145 (solid, 20 °C)  |
|                              |                          |                        | 0.310 (solid, 66.6 °C)      |                 |
| Erythritol                    | 118.0                    | 339.8                  | 0.326 (liquid, 140 °C)      | 1300 (liquid, 140 °C) |
|                              |                          |                        | 0.733 (solid, 20 °C)        | 1480 (solid, 20 °C)  |
| HDPE                          | 100–150                  | 200                    | n.a.                        | n.a.            |
| Trans-1,4-polybutadiene (TPB) | 145                      | 144                    | n.a.                        | n.a.            |

Table 2. Thermo-physical properties of salt hydrate PCMs [13-20]
5. Phase change materials for cooling

| Compound                  | Melting temperature (°C) | Heat of fusion (kJ/kg) | Thermal conductivity (W/m K) | Density (kg/m³) |
|---------------------------|--------------------------|------------------------|-----------------------------|-----------------|
| LiClO₃ · 3H₂O             | 8.1                      | 253                    | n.a.                        | 917 (solid, 0 °C) |
| ZnCl₂ · 2H₂O              | 10                       | n.a.                   | n.a.                        | 1720             |
| K₂HPO₄ · 6H₂O             | 13                       | n.a.                   | n.a.                        | n.a.             |
| NaOH · 2H₂O               | 15                       | n.a.                   | n.a.                        | n.a.             |
| Na₂CrO₄ · 10H₂O           | 18                       | n.a.                   | n.a.                        | n.a.             |
| KF · 4H₂O                 | 18.5                     | 231                    | n.a.                        | n.a.             |
| Mn(NO₃)₂ · 6H₂O           | 25.8                     | 125.9                  | n.a.                        | n.a.             |
| CaCl₂ · 6H₂O              | 29.2                     | 190.8                  | 0.540 (liquid, 38.7 °C)     | 1496 (liquid)    |
|                           | 29.2                     | 171                    | 0.561 (liquid, 61.2 °C)     | 1502 (liquid, 32 °C) |
|                           | 29.6                     | 174.4                  | 1.088 (solid, 23 °C)        | 1802 (solid, 24 °C) |
|                           | 29.7                     | 192                    |                             | 1710 (solid, 25 °C) |
|                           | 30                       |                        |                             | 1634             |
|                           | 29.39                    |                        |                             | 1620             |
| LiNO₃ · 3H₂O              | 30                       | 296                    | n.a.                        | n.a.             |
| Na₂SO₄ · 10H₂O            | 32.4                     | 254                    | 0.544                        | 1485 (solid)     |
|                           | 32                       | 251.1                  |                             | 1458             |
|                           | 31.32                    |                        |                             | n.a.             |
| Na₂CO₃ · 10H₂O            | 32.36                    | 246.5                  | n.a.                        | 1442             |
| CaBr₂ · 6H₂O              | 34                       | 247                    | n.a.                        | 156 (liquid, 35 °C) |
|                           | 36                       | 265                    | n.a.                        | 2194 (solid, 24 °C) |
| Na₃HPO₄ · 12H₂O           | 35.5                     | 280                    | n.a.                        | 1522             |
|                           | 35                       | 281                    |                             | n.a.             |
|                           | 35.2                     |                        |                             | n.a.             |
| Zn(NO₃)₂ · 6H₂O           | 36                       | 146.9                  | 0.464 (liquid, 39.9 °C)     | 1828 (liquid, 36 °C) |
|                           | 36.4                     | 147                    | 0.469 (liquid, 61.2 °C)     | 1937 (solid, 24 °C) |
|                           |                          |                        |                             | 2065 (solid, 14 °C) |
| KF · 2H₂O                 | 41.4                     | n.a.                   | n.a.                        | n.a.             |
| K₂(C₂H₃COO) · 1.5H₂O     | 42                       | n.a.                   | n.a.                        | n.a.             |
| K₃PO₄ · 7H₂O              | 45                       | n.a.                   | n.a.                        | n.a.             |
| Zn(NO₃)₂ · 4H₂O           | 45.5                     | n.a.                   | n.a.                        | n.a.             |
| Ca(NO₃)₂ · 4H₂O           | 42.7                     | n.a.                   | n.a.                        | n.a.             |
|                           | 47                       |                        |                             | n.a.             |
| Na₃HPO₄ · 7H₂O            | 48                       | n.a.                   | n.a.                        | n.a.             |
| Na₂S₂O₃ · 5H₂O            | 48.49                    | 201                    | n.a.                        | 1600 (solid)     |
|                           |                          | 209.3                  |                             | 1666             |
|                           |                          |                        |                             | 187              |
| Zn(NO₃)₂ · 3H₂O           | 54                       | n.a.                   | n.a.                        | n.a.             |
| NaOH · H₂O                | 58.0                     | 264                    | n.a.                        | 1450             |
| Na₂(CH₃COO) · 3H₂O        | 58.4                     | 226                    | n.a.                        | n.a.             |
| Cd(NO₃)₂ · 4H₂O           | 39.3                     | n.a.                   | n.a.                        | n.a.             |
| Fe(NO₃)₃ · 6H₂O           | 60                       | n.a.                   | n.a.                        | n.a.             |
| NaOH                     | 64.3                     | 227.6                  | n.a.                        | 1690             |
| Na₂B₂O₄ · 10H₂O           | 68.1                     | n.a.                   | n.a.                        | n.a.             |
| Na₃PO₄ · 12H₂O            | 69                       | n.a.                   | n.a.                        | n.a.             |
| Na₂P₂O₇ · 10H₂O           | 70                       | 184                    | n.a.                        | n.a.             |
| Ba(OH)₂ · 8H₂O           | 78                       | 265.7                  | 0.653 (liquid, 85.7 °C)     | 1937 (liquid, 84 °C) |
|                           |                          | 267                    | 0.678 (liquid, 98.2 °C)     | 2070 (solid, 24 °C) |
|                           |                          | 280                    | 1.255 (solid, 23 °C)        | 2180 (solid)     |
With the recently increasing requirements of the air-conditioning, it is becoming imperative to modernize cooling systems to become more cost-effective and eco-friendly. PCMs can be used in the making of cooling appliances meant for regulating the temperature of indoor areas. This implies that the PCMs must have the features of high energy density of melting, high latent heat value and low temperature range. Considerable amount of heat can be stored and discharged by the thermal energy storage by making use of the PCMs. The changes in the material phase are essential in this process. The process of melting and freezing (whereby the physical state of a material changes from solid to liquid or vice versa) absorbs or gives off heat energy. Material such as water, ice, paraffin, fat or inorganic salt can be used for this process. At fixed temperature, the change in physical form of a material may absorb or discharge considerable amount of latent heat. Consequently energy can be absorbed or discharged by making use of little temperature variation. Hence, the area of application determines the selection of the appropriate PCM. Different kinds and applications of PCMs for cooling purposes are discussed in this part of the research to enable the producer to consider various available materials with respect to the area of application.

5.1 Paraffin based materials
A mixture of hydrocarbon molecules forms a wax-like substance having no color, taste and smell. It is known as paraffin and is made from petroleum compounds and fossil fuels. The physical state of the paraffin is solid and it has a melting point of 37 °C and a density of 900 kg/m³. Some of the properties of the commercially-used paraffin are its insolubility in water and solubility in ether, benzene and some esters [21]. Moreover, the initial phase change temperature of the commercial paraffin is found to be 33.0 °C, the peak temperature is found to be 64.0 °C and the final temperature is found to be 70.0 °C and the latent heat is 140 kJ/kg.

5.2 Salt based materials
Compounds of sodium, potassium and lithium salt are some instances of salt-based materials. The latent heat of PCM and the sensible heat of both the solid and liquid phases can be preserved in these materials. In case of salt hydrates, latent heat contributes to a major portion of stored heat. Different attributes of a salt including its concentration, size and shape determine its thermal conductivity. But, energy storage density will be reduced as a consequence of higher concentration of thermal conductivity enhancer. Hence, certain applications require equilibrium between thermal conductivity and the required energy storage density, [22]. The thermal conductivity is directly proportional to the quantity of carbon in the compound. Carbonate molten salt (LiNaCO₃) may be present in the used PCM. It is basically made by the reaction between sodium carbonate (Na₂CO₃) and lithium carbonate (Li₂CO₃) and is round in shape with a smooth surface. The surface of PCMs may also contain some nano-particles. Although water and other organic solvents have the potential to wet the Graphite due to its surface tension, the probability of graphite wetting by the liquid molten salts is very low. The physical and chemical stability and the thermal conductivity can be increased by using eutectic salt of lithium and sodium carbonates as PCM, magnesium oxide as ceramic and carbon allotropes as thermal conductivity enhancer. The structure of the compound is developed by the wettability of salt while; poor salt wettability results in swelling of the compound structure. Therefore, in these processes, it is imperative to maintain balance to ensure improved properties and actions of compounds. When nano-material is introduced, it results in the creation of nano-layer due to the large specific surface area of the nano-material which implies that the PCM specific heat can be improved by the nano-material [23]. Higher surface energy is generated by the large specific surface area. This energy supports the accumulation of nano-material resulting in formation of blocks of nano-material. Nano-material surface area is reduced due to the accumulation of nano-particles which causes deterioration in the developments caused by LiNaCO₃. A couple of factors affect the specific heat; the specific heat is enhanced by the nano-layer creation and reduced by the accumulation of nano-material. Lithium carbonate is refined by reducing its solubility in hot water in order to improve its properties. Electrolysis of potassium chloride is conducted to yield Potassium hydroxide which is made to react with CO₂ to yield potassium carbonate. Among the main uses of KHCO₃ are the balancing of neurons, formation of welding fluxes and flux coating and preparation of farm animals’ food to fulfill their
dietary potassium needs. An increase in atmospheric pressure makes the hydrogen bonds even stronger in KHCO₃. However, Hydrogen atoms in the molecule of KHCO₃ may also repel each other and result in amorphousization under the influence of high pressure. The hydrogen bond may break as the angle between two oxygen atoms gets bigger under the influence of increased pressure of 2.8GPa.

5.3 Graphene based materials
Graphene contains a 2D sheet with carbon bonding. It contains a layer of graphite in which interaction between the molecules is supported by Van Der Waal forces. Oxidation of graphite yields graphene [24]. In case the graphene sheet is less than 20 nano-meters thick, the graphene produced is not stable and converts into a highly stable compound called fullerene. The main features of the graphene are that it is a good conductor of heat and electricity and has high Young’s modulus. Moreover, it has a soft membrane. There is no band-gap in single-layered graphene with almost 97.7% optical transmittance. Graphene has a surface area of 2600 m²/g. The experts carried out wide spread research on Nano-electronics, fuel-cells, super capacitors, gas adsorption, separation, storage, batteries, catalysis and sensing because of the major properties of graphene. A couple of oxygen-containing functional groups are included in the graphene oxide structure. The ends of graphene sheets contain hydroxide and epoxide groups and carbonyl and carboxyl groups [24]. Graphene oxide is highly soluble in most of the solvents including water. The benefits of gas adsorption, storage and separation in functional area can be acquired by the flaws on graphene sheet produced as a result of the reduction and oxidation of graphene. The high abundance, strong pore structure, low weight and stability of Carbon based materials allow their usage for gas adsorption, preservation and separation. Moreover, carbon based materials are economical and can be scaled up conveniently. High temperature chemical adsorption and low temperature physical adsorption of H₂, CO₂, CH₄, etc can be conducted using Graphene based compounds. The thermal conductivity of suspended Graphene at room temperature is 5300 W/m·K, which is significantly higher as compared to the thermal conductivity of pyrolytic graphite (2000 W/m·K). Thermal conductivity of Graphene can be improved by the expanded graphite. When pristine EG flakes are subjected to constant voltage, there is an unexpected fluctuation in temperature followed by equilibrium; however, the temperature quickly returns back to room temperature when the voltage is removed. Hence, a phase change process is characterized by the storage and discharge of heat energy on the application and removal of voltage. This can be attributed to the fluctuation in composite temperature with changes in voltage.

5.4 Foam based materials
The infiltration method is used to manufacture the foam based PCMs, having a porosity of 62–72%. The resulting pores are smaller than 1 mm and their density is 103 kg/m³. The most favorable materials to be installed in buildings to conserve energy and to ensure solar energy preservation are the paraffin wax and the Stearic acid because of their temperature fluctuation and latent heat values during the phase change process. Paraffin is produced from slack wax. Slack wax is comprised of oil and wax. The main source of slack wax is the process of refining of lubricant which yields slack wax as a by-product. The crystalline features of the paraffin wax are adapted by slack wax. The saponification of oil and wax with 200 °C hot water yields Stearic acid. The initial temperature of stearic acid is 54.7 °C and its final phase change temperature is 70.6 °C [25]. Stearic acid has a latent heat equal to 141kJ/kg. Significant values of latent heat storage capacity is depicted by these shape-wise stable PCMs or foam compounds. This can be attributed to their exceptional-compressing yield potential, high-quality interface, ideal phase change temperature range and latent heat values. Certain polymer based materials including polyethylene glycol helps in the manufacturing and application of porous foams installed with PCM for thermal storage. Polyethylene glycol can be classified as: the shorter polyethylene glycols and the longer ones. Lesser sub cooling and wide range of melting temperature are associated with shorter polyethylene glycols having M < 1000 , while the longer polyethylene glycols provide greater amount of sub cooling [26]. The longer polyethylene glycols are characterized with M > 4000 and they depict smaller range of the melting point. Longer polyethylene glycols have greater latent heat or melting enthalpy.

6. Applications of phase change materials for cooling
The application of PCMs for cooling purposes in buildings was devised with the help of various reliable researches. The PCM may be applied for cooling in buildings in many ways including PCMs installation in walls [27-34], PCMs installation in roofs [31,35,36], PCMs installation in flooring [37], PCMs combination with bricks [33, 38], and PCMs enabling ventilation[39,40]. It was found that 60% of the researches involved the PCMs in the walls using the encapsulation technology. It was noticed also, that the indoor temperature can be cooled by 2-5 ºC for almost 2-3 hours during the daytime. A PCM installed building depicts 20-30% lesser cooling load as compared to other buildings in similar climatic conditions. Usually, salt based compounds are used as PCMs for cooling purposes [41].

7. Conclusions
This study reveals that the characteristics of the PCMs such as their melting point, latent heat, stability and threshold of sub-cooling play an important part in the classification of PCMs used for cooling. The advantages and disadvantages of each PCM were revealed after thoroughly reviewing the diverse kinds, features and applications of PCMs. The most common advantages of the PCM include latent heat, reasonable melting point and low vapor pressure, whereas low thermal conductivity, volume variation and solubility are identified as the disadvantages of most PCMs. PCMs are the subject of interest for most researchers and has the potential to transform the field of engineering and to ensure eco-friendly energy sources.

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