Design and Analysis of Phase Change Material based thermal energy storage for active building cooling: a Review

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ABSTRACT

Phase Change Materials (PCMs) are "latent" thermal storage materials. They use chemical bonds to store and release heat. The thermal energy transfer occurs when a material changes from a solid to a liquid or from a liquid to a solid form. This is called a change in state or "phase." Initially, these solid-liquid PCMs perform like conventional storage materials; their temperature rises as they absorb solar heat. Unlike conventional heat storage materials, when PCMs reach the temperature at which they change phase (their melting point), they absorb large amounts of heat without getting hotter. When the ambient temperature in the space around the PCM material drops, the Phase Change Material solidifies, releasing its stored latent heat. PCMs absorb and emit heat while maintaining a nearly constant temperature. Within the human comfort and electronic-equipment tolerance range of 20°C to 35°C, latent thermal storage materials are very effective. They can be used for equalization of day & night temperature and for transport of refrigerated products. In the proposed project heat of fusion of CaCl2. 6H2o as PCM is used for cooling water during night and this cooled water is used as circulating medium trough fan coil unit, air trough FCU will get cooled by transferring heat to water and fresh & cool air will be thrown in a room. In the proposed project FREE COOLING & ACTIVE BUILDING COOLING concepts of Thermal Energy Storage are used in combine

Keywords: Free cooling, phase change material, cooling towers, LHTES. Active building cooling

Introduction

In this proposed work of experiment, free night time cooling system is used for Cooling water and PCM (CaCl2. 6H2O) with the help of cooling tower.

In this experimental set upPCM latent heat cool energy storage can be provided with water by utilizing conventional water cooling towers which helps to cool the circulating water. during night shutters are opened and also a cooling tower pump is also in on mode so that a free flowing ambient air comes in contact with cooling tower water which cools the water to the desirable range of 150C TO 200C, when this cooled water reaches to TES tank absorbs heat from the PCM and lowering its temperature to its freezing point. At this point PCM absorbs the latent heat without lowering its temperature further. This cooled water is used to circulate through a fan coil unit during day period for cooling the room. Again this latent heat of PCM maintains the low temperature of circulating water.

By storing over-night cool energy for day-time cooling requirements in summer, a PCM system can simply bridge the gap between energy availability and energy use and therefore has the potential to achieve considerable environmental as well as economical benefits for many heating and cooling applications. Using PCM’s for storage of latent heat is extremely economical, as the cost for air conditioning systems (installation and running cost) can be significantly reduced. At night the cooling tower produce conventional 18°C cool water which passes to the TES tank in order to charge the system. The cooling effect from the chilled water is absorbed by the phase change material thereby freezing the eutectic solution at its phase change point.
During the day, warm returned water from the fan coil unit flows to the TES tank to recover the stored latent heat capacity of the phase change materials before returning the fan coil unit. This system is easy to operate and control due to its static nature of the design and it is considered to be practicality maintenance-free.

The advantages of this system are

- System is free from ozone depletion potential and global warming potential unlike refrigerator and air conditioner.
- Systems provide the potential to attain the energy saving which reduce the environment impact.
- Systems meet the need of cooling at low cost.
- Electricity consuming components such as compressor unit of air conditioning unit is eliminated in this system.

Phase Change Material

Phase Change Material (PCM) is a substance with a high heat of fusion which, melting and solidifying at certain temperatures, is capable of storing or releasing large amounts of energy. Phase change materials are latent heat storage substance, in which energy is store in the process of changing the state i.e. either by solid to liquid or liquid to solid. When phase change materials attain the temperature at which phase change occur, they absorb large amount of energy and phase change material solidifies, releasing its stored latent heat when the ambient temperature around phase change material drops. According to M. Fatih Demirbas .The amount of heat energy that can be stored in phase change material is estimated by,

\[
\text{Heat energy (Q)} = \text{(change in temperature)} \times \text{(mass)} \times \text{(specific heat)}.
\]

Required properties for phase change material.

1. **Release and absorb large amounts of energy when freezing and melting;** this requires the PCM to have a large latent heat of fusion and to be as dense as possible

2. **Have a fixed and clearly determined phase change temperature (freeze/melt point);** The PCM needs to freeze and melt cleanly over as small a temperature range as possible. Water is ideal in this respect, since it freezes and melts at exactly 0°C (32°F). However many PCMs freeze or melt over a range of several degrees, and will often have a melting point that is slightly higher or lower than the freezing point. This phenomenon is known as hysteresis.

3. **Avoid excessive super cooling;** Super cooling is observed with many eutectic solutions and salt hydrates. The PCM in its liquid state can be cooled below its freezing point whilst remaining a liquid.

4. **Remain stable and unchanged over many freeze/melt cycles;** PCMs are usually used many times over, and often have an operational lifespan of many years in which they will be subjected to thousands of freeze/melt cycles. It is very important that the PCM is not prone to chemical or physical degradation over time which will the energy storage capability of the PCM.

5. **Non-hazardous;** PCMs are often used in applications whereby they could come in contact with people, for example in food cooling or heating applications, or in building temperature maintenance. For this reason they should be safe.

6. **Economical;** It doesn't matter how well a substance can perform as a PCM if is prohibitively expensive. PCMs can range in price from very cheap (e.g. water) to very expensive (e.g. pure linear hydrocarbons). If cost outweighs the benefits obtained using the PCM, its use will be very limited.

Types of Phase Change Material

PCM may be organic or inorganic materials. The phase changes comprise predominantly solid-liquid transitions for thermal storage applications.
(I) Inorganic PCM

These materials are salt hydrates, the phase change properties of these materials are shown in Table 1. These PCMs have some attractive properties including high latent heat values, they are not flammable and their high water content means that they are inexpensive and readily available. However, their unsuitable characteristics have led to the investigation of organic PCMs for this purpose. These include corrosiveness; instability, improper re-solidification, and a tendency to super cool.

Table 1: Salt hydrate PCMs (typical values)

<table>
<thead>
<tr>
<th>Phase change material</th>
<th>Melting point (°C)</th>
<th>Heat of fusion (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF.4H2O Potassium fluoride tetra hydrate</td>
<td>18.5</td>
<td>231</td>
</tr>
<tr>
<td>Mn(NO3)2.6H2O Manganese nitrate hexahydrate</td>
<td>25.8</td>
<td>125.9</td>
</tr>
<tr>
<td>CaCl2.6H2O Calcium chloride hexahydrate</td>
<td>29.0</td>
<td>190.8</td>
</tr>
<tr>
<td>CaBr2.6H2O Calcium bromide hexahydrate</td>
<td>30.2</td>
<td>115.5</td>
</tr>
<tr>
<td>Li NO3.6H2O Lithium nitrate hexahydrate</td>
<td>30.0</td>
<td>296</td>
</tr>
<tr>
<td>Na2SO4.10H2O Sodium sulphate decahydrate</td>
<td>32.4</td>
<td>254</td>
</tr>
<tr>
<td>Na2CO3.10H2O Sodium carbonate decahydrate</td>
<td>34.2</td>
<td>146.9</td>
</tr>
<tr>
<td>Na2HPO4.12H2O Sodium orthophosphate dodecahydrate</td>
<td>35.5</td>
<td>265</td>
</tr>
<tr>
<td>Zn(NO3)2.6H2O Zinc nitrate hexahydrate</td>
<td>36.2</td>
<td>246.5</td>
</tr>
</tbody>
</table>

(ii) Organic PCMs

Organic PCMs have a number of characteristics which render them useful for latent heat storage. They are more chemically stable than inorganic substances, they melt congruently and super cooling does not pose as a significant problem. Although the initial cost of organic PCMs is higher than that of the inorganic type, the installed cost is competitive. However, these organic materials do have their quota of unsuitable properties. Of the most significant of these characteristics, they are flammable and they may generate harmful fumes on combustion. Other problems, which can arise in a minority of cases, are a reaction with the products of hydration in concrete, thermal oxidative ageing, odour and an appreciable volume change. The most promising selection of these organic PCMs is shown in Table 2.
Table 2: Salt hydrate PCMs (typical values)

<table>
<thead>
<tr>
<th>Phase change material</th>
<th>Melting point (°C)</th>
<th>Heat of fusion (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃(CH₂)₁₆COO(CH₂)₃CH₃ Butyl stearate</td>
<td>19</td>
<td>140</td>
</tr>
<tr>
<td>CH₃(CH₂)₁₁OH 1-dodecanol</td>
<td>26</td>
<td>200</td>
</tr>
<tr>
<td>CH₃(CH₂)₁₂OH 1-tetradecanol</td>
<td>38</td>
<td>205</td>
</tr>
<tr>
<td>CH₃(CH₂)n (CH₃...Paraffin</td>
<td>20-60</td>
<td>200</td>
</tr>
<tr>
<td>45% CH₃(CH₂)₈COOH 55% CH₃(CH₂)₁₀COOH 45/55 capric-lauric acid</td>
<td>21</td>
<td>143</td>
</tr>
<tr>
<td>CH₃(CH₂)₁₂COOC₃H₇ Propyl palmitate</td>
<td>19</td>
<td>186</td>
</tr>
</tbody>
</table>

Selection of PCM

In order to select the best qualified PCM as a storage media some criteria’s are mentioned. (Furbo and Svendsen (1977)).

According to thermal properties,
- the melting point of the PCM must be lying in a practical range of operation. Temperature interval going from 25 °C to 70 °C,
- the latent heat should be as high as possible to minimize the physical size of the heat storage.
- a high thermal conductivity would assist the charging and discharging of the energy storage.

According to chemical properties, a suitable PCM should be non toxic, non flammable, non dangerous, non corrosive and long term chemical stable.

According to physical properties, it must have limited changes in density to avoid problems with the storage tank, low vapour pressure, favorable phase equilibrium.

Moreover PCM must be available in large quantities, cheap in order to make the system economically feasible.

Considering all above properties and average annual temperature range for Nagpur city as given in table 3

Table 3: An average temp range 2010

<table>
<thead>
<tr>
<th>Month</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>12.4</td>
<td>15</td>
<td>19</td>
<td>23.9</td>
<td>27.9</td>
<td>26.3</td>
<td>24.1</td>
<td>23.6</td>
<td>22.9</td>
<td>19.8</td>
<td>14.9</td>
<td>12.1</td>
</tr>
<tr>
<td>Max</td>
<td>28.6</td>
<td>32.1</td>
<td>36.3</td>
<td>40.2</td>
<td>42.6</td>
<td>37.8</td>
<td>31.5</td>
<td>30.4</td>
<td>31.8</td>
<td>32.6</td>
<td>30.4</td>
<td>28.2</td>
</tr>
</tbody>
</table>

CaCl₂.6H₂O (calcium chloride hexa-hydrate) is most suitable for climatic conditions of Nagpur city; it is easily available, economical, non-toxic, non-dangerous, non-corrosive, and chemically stable.

It have limited changes in density to avoid problems with the storage tank, low vapour pressure, favorable phase equilibrium.

Thermo-chemical properties of CaCl₂.6H₂O (calcium chloride hexa-hydrate) are given in table 4
Table 4: thermo-physical properties of cacl2.6h2o with some additives

<table>
<thead>
<tr>
<th>Description</th>
<th>Viscous Semi-Solid near Phase Change Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Translucent</td>
</tr>
<tr>
<td>Base Material</td>
<td>Inorganic Salts</td>
</tr>
<tr>
<td>Phase Change Temperature</td>
<td>28-30°C</td>
</tr>
<tr>
<td>Sub Cooling</td>
<td>2°C max</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.48-1.50</td>
</tr>
<tr>
<td>Latent Heat Practically</td>
<td>175 Joules/g</td>
</tr>
<tr>
<td>Latent Heat Theoretical</td>
<td>188 Joules/g</td>
</tr>
<tr>
<td>Spec. Heat</td>
<td>2 Joules/g °C</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>1Watt/m °C</td>
</tr>
<tr>
<td>Congruent Melting</td>
<td>Yes</td>
</tr>
<tr>
<td>Flammability</td>
<td>No</td>
</tr>
<tr>
<td>Hazardous</td>
<td>No</td>
</tr>
<tr>
<td>Thermal Stability</td>
<td>&gt; 10000 cycles</td>
</tr>
<tr>
<td>Max. Operating Temperature</td>
<td>100°C</td>
</tr>
</tbody>
</table>

**Binary Phase diagram: The Calcium Chloride-water system**

Pure water freezes to ice at 0°C. If CaCl2 or another solute is added to water, the freezing point of the solution will be lower than 0°C. As the graph below shows, ice will form at -20°C in a 20 mass % solution of CaCl2. This phenomenon is called a freezing point depression. It can be explained from changes in chemical potentials.
Figure indicates the binary phase diagram of calcium chloride and water. The hexahydrate contains 50.66 wt% CaCl2 and the tetra hydrate 60.63 wt%. The melting point of the hexahydrate is 29.6 °C, with that of the tetra hydrate being 45.3 °C. The hexahydrate-α Tetra hydrate peritectic point is at 49.62 wt% CaCl2-50.38 wt% H2O, and 29.45 °C. In addition to the stable form, there are two monotropic polymorphs of the tetra hydrate salt, β and γ. The latter two are rarely encountered when dealing with the hexahydrate composition;

However, the α tetra hydrate is stable from its liquids temperature, 32.78 °C, down to the Peritectic point, 29.45 °C, thus showing a span of 3.33 °C. When liquid CaCl6.6H2O is cooled at the equilibrium, CaCl2.4H2O can begin to crystallize at 32.78 ºC. When the peritectic is reached at 29.45 ºC, the tetra hydrate hydrates further to form hexahydrate, and the material Freezes. The maximum amount of tetra hydrate which can be formed is 9.45 wt%, calculated by the lever rule. This process is reversed when solid CaCl6.6H2O is heated at the Equilibrium. At 29.45 ºC the peritectic reaction occurs, forming 9.45% of CaCl2.4H2O and the liquid of the peritectic composition. With increasing temperature, the tetra hydrate melts, disappearing completely at 32.78 ºC. Under actual freezing and melting conditions, the

Equilibrium processes described above may occur only partially or not at all. Super cooling of the tetra hydrate may lead to initial crystallization of the hexahydrate at 29.6 °C (or lower if this phases also super cools). It is possible to conduct modification by additives. From a number of potential candidates, Ba (OH) 2, BaCO3 and Sr (OH) 2 were chosen as they seemed to be feasible. When we used Ba(OH)2 and Sr(OH)2 at 1% part by weight, there was no Super cooling. We were able to increase the stability of the equilibrium condition by adding KCl (2 wt %) and NaCl, Figure 8. NaCl is a weak soluble in CaCl2.6H2O, therefore the part by weight is only about 0.5
Experimental set up:

Fig – Cac12.6H2o based TES System for active building cooling purpose

Aim of this project is to use the latent heat energy storage of phase change materials (Cac12. 6H2o) for room cooling. In the proposed project heat of fusion of Cac12. 6H2o as PCM is used for cooling water during night and this cooled water is used as circulating medium trough fan coil unit, air trough FCU will get cooled by transferring heat to water and fresh & cool air will be thrown in a room.

In the proposed project FREE COOLING & ACTIVE BUILDING COOLING concepts of Thermal Energy Storage are used in combine.

* Free /Night Cooling – According to free/Night cooling concept PCM Material is allowed to change its phase by atmospheric temperature fall during night, which will absorb & store the thermal energy for later use.

* Active Building Cooling – According to this concept energy stored during charging mode (night) will be used to cool the air (discharging mode) entering in room.

Working of Project:

Experimental set up mainly consist of three parts.

**TES Tank** – Thermal energy tank consist of a PCM (Cac12. 6H2o) plastic envelopes kept in a plastic trays. These trays are immersed in water hence heat transfer between water & PCM is possible.

**Cooler cum Cooling Tower** – If the FCU becomes ineffective during summer mid days at that time this part will act as a dessert cooler otherwise it will continue to act as a cooling tower (24x7).

**Fan Coil Unit** – Fan coil unit consist of copper coils through which cooled water circulates which cools the circulating air flowing over the coil.

Water pump will be ON continuously 24x7 and hence water flowing along the walls of water cooler will come in contact with the air and water will get cooled because of evaporation. This cooled water is flown to TES tank and same heat is stored by the Cac12.6H2O. When temperature reaches below phase change temperature of Cac12.6H2O, It becomes crystalline solid. This phase change will surely happen during charging mode (night) and will continue to provide cool water during discharging mode (day) when FCU is switched ON.

During mid summer days when FCU will be ineffective at that time dessert cooler can be switched on after shifting the water circulation flow to dessert cooler through three way arrangement. In this way flexibility and balancing between the desserts cooler and Air conditioning can be achieved.
Results:

- Energy consumption and costs is reduced by 40%,
- Indoor air quality is improved as humidity control is possible,
- Flexibility of operation is increased,
- Maintenance cost [as compressor of air conditioning systems is eliminated] is reduced,
- Will help to conserve fuel and burning of fossil fuels to produce energy.
- GHG, CFC emissions will be reduced.

Conclusion

Thermal energy storage by using Phase change material like CaCl2.6H2O is a prominent technique for building cooling purposes. Due to its required melting temperature i.e. 28-30 °C respectively and its high heat of fusion, also CaCl2.6H2O has good physical properties such as large thermal conductivity, high density, stability. All these properties made it as a prominent phase change material.

This experimental set-up provide a good product to tackle the humidity problem by dessert coolers, an energy saving, eco-friendly and economical equipment.

Acknowledgment

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