Experimental study of supercooling and \( p_{\text{H}} \) behaviour of a typical phase change material for thermal energy storage

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Thermal energy storage plays an important role in the storage of available energy and hence, improves its utilization during odd hours especially, in the presence of an intermittent heat source. Phase change materials (PCMs) also play very important role in thermal energy storage due to their qualities to store more heat in small volume. But there are some disadvantages in most of the inorganic PCMs, such as fluctuation in their normal freezing point, known as supercooling behaviour. There are certain additives that play an important role in minimizing and/or removing the supercooling behaviour of different PCMs. In the present study, the supercooling behaviour of a typical PCM and the effect of \( p_{\text{H}} \) value have been studied. The results obtained through experimental study have been compared with those obtained through differential scanning calorimeter (DSC) and found to be in good agreement with each other.

**Keywords:** Thermal energy storage, Phase change materials, Supercooling, Differential scanning calorimeter

1 Introduction

Phase change materials play a very important role in the thermal energy storage and heating and cooling applications. Nowadays, a number of phase change materials (PCMs) both organic and inorganic are available in the market depending on the requirement of melting and freezing points. As some of the energy sources are intermittent in nature, both the short and long term thermal energy storage are essential for most of the applications. Both long and short term thermal energy storage are equally important for useful applications such as heating and cooling of buildings, space air-conditioning, power generation and so on. There are various thermal energy storage methods, but the latent heat storage is the most attractive due to the high storage density and a small temperature variation for its retrieval. The application of thermal energy storage includes solar energy, greenhouse agricultural, temperature regulating in textile, heat management of electronic and telecommunication equipments, heating and cooling, and space air-conditioning applications\(^3\).

The use of PCMs for construction of thermal energy storage has been a subject of considerable interest for the last few decades, due to their interesting feature to store both the latent heat and the sensible heat. As a PCM absorbs heat, its phase change from solid to liquid and/or liquid to gas while its temperature almost remains constant. On the other hand when PCMs releases heat the temperature again remains constant but its phase changes from liquid to solid and/or gas to liquid. The heat absorbed or released during these processes is a physical phenomenon and since the temperature is nearly constant during these processes, it is also known as isothermal (heating and cooling) energy storage. The materials to be used for thermal energy storage must exhibit some physical, chemical and thermal properties such as a large latent heat and high thermal conductivity.

A PCM should have a melting temperature lying in the practical range of operations depending on the requirement of a particular application. For example, it should melt congruently with minimum supercooling and it must be chemically stable, cheaper, and easily available besides, it must be non toxic and non corrosive. The materials that have been studied during the last four decades are hydrated salts, paraffin waxes, fatty acids and eutectics of organic and inorganic compounds. Latent heat storage medium such as inorganic salts and organic materials are more attractive than those of the sensible heat storage medium due to the fact that the former has higher heat storage density and a narrower temperature range for the heat storage and recovery cycles, while it is reverse in the case of later\(^2\).
inorganic salt hydrates as latent heat storage materials have certain advantages over the organic materials in the same melting temperature range. The salt hydrates among the PCMs usually have high latent storage densities, and they are non-flammable because of lower vapour pressure. However, practical difficulties usually arise in the use of PCMs due to the low thermal conductivity, density variations, instability of properties under extended cycling and sometimes phase segregation, especially, in salt hydrates and supercooling.

Among the above mentioned materials, hydrated salts in general, are the most attractive materials for thermal energy storage due to their high volumetric storage density, relatively high thermal conductivity, and moderate costs as compared to paraffin waxes, with few exceptions. Besides, the temperature remains nearly constant during the phase change, which is beneficial for both the supply and demand, especially, for active and passive heating/cooling and space air-conditioning applications. The previously researched (PCM) salt hydrates are made of calcium chloride hexahydrate (CaCl$_2$.6H$_2$O) and possess a very high storage capacity due to a comparatively high density but there are some crucial disadvantages such as supercooling and phase instability. A number of researchers have used the hydrated salts in direct contact heat transfer between the immiscible heat transfer fluid and the hydrated salt solution. Some of the hydrated salts studied so far include Na$_2$SO$_4$.10H$_2$O, Na$_2$HPO$_4$.12H$_2$O, NaCO$_3$.10H$_2$O, and Na$_2$S$_2$O$_3$.5H$_2$O. These salts are generally, either acidic or alkaline in nature besides; they react with certain types of containers, so it is very important to neutralize them before being used in thermal energy storage.

In spite of the problems associated with hydrated salts, non-agitated thermal energy storage materials have been preferred. Nagano et al. investigated the phase change materials in the temperature range of 60-90°C. They studied a particular PCM viz. magnesium nitrate hexahydrate using a suitable additive to regulate the melting point. The addition of 5-10 weight percentage of the additive resulted in a regulated melting point of around 80°C and the heat of fusion of about 150 kJ/kg. Nagano et al. also found that the increasing mix ratio has a little effect on the heat of fusion, while it has a significant effect on the melting point. The repeated melting and solidification tests showed that the heat of fusion and melting point retained their original values after 1000 cycles. Ryu et al. have performed extensive study on suitable thickening and nucleating agents, which can be used for a number of hydrated salts. Sari and Karaipkli studied the thermal conductivity and latent heat storage characteristics of paraffin/expended graphite composite as PCM through differential scanning calorimeter (DSC) analysis. They observed that by increasing the thermal conductivity, the melting time decreases. They also found that the variation in melting temperature is negligible and the latent heat was observed approximately equal to the original value of the mixture.

In the present study, the degree of super heating and the variation of pH value on the thermo-physical properties of calcium chloride hexahydrate (CaCl$_2$.6H$_2$O) has been carried out because it is easily available in the market and has low cost than those of the other PCMs salts. The latent heat of CaCl$_2$.6H$_2$O is very high and the normal freezing temperature is 24°C, which make it suitable for the use in building heating/cooling and space air-conditioning applications. But it has a disadvantage of supercooling, besides, it is acidic in nature.

2 Experimental Details

In the present study, commercial grade CaCl$_2$.6H$_2$O salt was chosen and the necessary pH balance was done using laboratory grade NaOH. The experiment for the repeated hundred melt-freeze cycles has been conducted in the laboratory to study the supercooiling behaviour at different pH values and the latent heat of fusion was studied through DSC. The experimental setup consists of a constant temperature unit, thermocouples and data acquisition unit attached with a PC for analysis. The constant temperature set-up with cold and hot water unit has a temperature range of 0 to 35°C with resolution of ±0.1°C (Fig. 1). Calibrated J-type thermocouples were used to measure the temperature. In one side of the setup there was a transparent glass window to check the physical state (phase) of the PCM. The experimental study was divided into two parts (i) to balance the pH and (ii) to remove/minimize the supercooling. The latent heat of fusion and the melting temperature were also measured by DSC (Q-100) TA Instrument USA, using an additive after 1st, 25th, 50th and 100th cycles. The properties of the present chemical and the specifications of the instrument are given in Table 1 and the results for different melt-freeze cycles by DSC are given in Table 2, while the photographic view of the instrument is shown in Fig. 2.
2.1 Balancing of pH

A 25 ml sample of CaCl$_2$.6H$_2$O at room temperature was taken and NaOH solution was used to attain a pH of 7.0 in steps for four different samples as below:

i) pH 5.3 (initial),
ii) pH adjusted to 6.0,
iii) pH adjusted to 6.5, and
iv) pH adjusted to 7.0.

All four samples, mentioned above, have been categorized as pH 5.3, pH 6.0, pH 6.5, and pH 7.0, respectively. After adjusting the pH value, all the samples were used for cycle testing from 1 to 100 cycles and the supercooling behaviour was analyzed and the results of 1$^{st}$, 25$^{th}$, 50$^{th}$, 100$^{th}$ cycle are shown on the respective graphs in Figs 3-10. In order to remove and/or minimize the supercooling of CaCl$_2$.6H$_2$O, the experiment was repeated for total two hundred heating and cooling cycles into two steps viz. one hundred cycles with additive and another hundred cycles without additive. The study of all the four samples without additive for one hundred cycles and with a variable weight percentage of the additive for another hundred cycles have been carried out thoroughly and the results were compared with those obtained through DSC analysis.

3 Results and Discussion

3.1 Without additive

The pH value of CaCl$_2$.6H$_2$O was balanced using NaOH solution in all four samples taking initial pH value of 5.3 and has been analyzed up to 100 cycles. Each sample exhibits different behaviour after each cycle and the results of four different melting and freezing (1$^{st}$, 25$^{th}$, 50$^{th}$ and 100$^{th}$) cycles are shown in their respective figures.
Fig. 3 — Variation in freezing temperature of CaCl$_2$·6H$_2$O without additive at different pH values after 1$^{st}$ melt-freeze cycle.

Fig. 4 — Variation in freezing temperature of CaCl$_2$·6H$_2$O without additive at different pH values after 25$^{th}$ melt-freeze cycle.
Fig. 5 — Variation in freezing temperature of CaCl\textsubscript{2}.6H\textsubscript{2}O without additive at different pH values after 50\textsuperscript{th} melt-freeze cycle

Fig. 6 — Variation in freezing temperature of CaCl\textsubscript{2}.6H\textsubscript{2}O without additive at different pH values after 100\textsuperscript{th} melt-freeze cycle
Fig. 7 — Variation in freezing temperature of CaCl₂·6H₂O with additive at different pH values after 1ˢᵗ melt-freeze cycle

Fig. 8 — Variation in freezing temperature of CaCl₂·6H₂O with additive at different pH values after 25ᵗʰ melt-freeze cycle
Fig. 9 — Variation in freezing temperature of CaCl$_2$.6H$_2$O with additive at different pH values after 50$^{th}$ melt-freeze cycle

Fig. 10 — Variation in freezing temperature of CaCl$_2$.6H$_2$O with additive at different pH values after 100$^{th}$ melt-freeze cycle
To study the melting-freezing behaviour of different samples, the temperature of the experimental unit was set at 20°C for the first cycle. As can be seen from Fig. 3 that sample with pH 5.3 freezes at 24.4°C while sample with pH 6.0, pH 6.5 and pH 7.0 could not be freeze. The temperature of the setup was further decreased up to 15, 10 and 0°C to solidify other samples with pH 6.0, pH 6.5 and pH 7.0. These samples were in the liquid phase up to temperature of 7.8, 5.2 and 6.2°C, respectively but as their temperatures further decrease all the samples solidify simultaneously. The result of all samples with

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10.1 °C and 1.2°C after 100 cycles (Figs 5-6). As a result, sample with pH 5.3 found to be 23.5°C, for sample of pH 6.0 was found to be 24.5°C, for sample with pH 6.5 was found to be 23.5°C and for sample with pH 7.0 was found to be 24°C, respectively, as can be seen from Fig. 8. The results shown in Fig. 8, exhibit that the supercooling still exists in all the four samples and hence, the weight percentage of additive has not yet reached the optimum value of the total weight of PCM. That is why all the four samples have fluctuation in the freezing point, i.e. these samples solidify at different temperatures. However, this fluctuation in the freezing points of different samples is not very high and hence, can be minimized further by using the suitable weight percentage of the additive in all the four samples.

In the last two experiments, the weight percentage of the additive was increased by a significant amount in two parts and has been tested for 50 and 100 cycles. The samples tested for 50 cycles have less weight percentage of the additive while it was more in all samples used for 100 cycles. The results for 50 cycles are shown in Fig. 9, while the results for 100 cycles are shown in Fig. 10. It can be seen that the freezing point of four samples with pH values of 5.3, 6.0, 6.5 and 7.0, respectively, were found to be 23.8, 24, 24.2 and 24.5°C after 50th cycle as can be seen from Fig. 9. On the other hand, the freezing point of all the four samples were found to be 23.9, 24, 24.1 and 24.2°C, respectively, after 100th cycle, as can be seen from Fig. 10. Thus the freezing point of all four samples after 50th and 100th cycles are very closed to each other, besides, all the samples after 100th cycles solidify at a temperature very closed to one another irrespective of their pH values, as can be seen from Figs 9-10. In other words, the supercooling in all the samples with pH 5.3, pH 6.0, pH 6.5 and pH 7.0 is all most negligible. It means the supercooling from CaCl₂·6H₂O after mixing a suitable weight percentage of the additive has been minimized in this particular study.
All the samples after certain (1\textsuperscript{st}, 25\textsuperscript{th}, 50\textsuperscript{th} and 100\textsuperscript{th}) cycles were tested for measuring the latent heat and freezing points using DSC. The results obtained through DSC tests were found to be very close to those of the experimental results, which is a strong point to verify that the experimental analysis has been conducted with the best possible precautions. The latent heat and melting temperatures of all the samples obtained through DSC are given in Table 2. It is observed that the experimental results are in good agreement with those obtained through DSC tests. The experimental study carried out in the present work has been very useful in the removal and/or minimizing the supercooling of CaCl\textsubscript{2}.6H\textsubscript{2}O with the mixing of an additive in the optimum weight percentage for applications in the thermal energy storage.

4 Conclusions
The supercooling behaviour of a typical PCM and the comparative effect of different pH values with and without additive has been presented. The results of all samples after melting freezing testing cycle show different behaviour, it means the supercooling exist in all the samples without additive. It can be seen that the freezing of all four samples after hundred cycles is found to be stable with certain weight percentage of the additive. This particular result exhibits that there is almost no supercooling as all the samples freeze at almost the same temperature. Hence, it can be concluded that the optimum percentage weight of the additive plays a very important role in removal and/or minimizing the supercooling of any phase change material to be used in the application of the thermal energy storage. All the samples after certain cycles were tested through DSC and the latent heat and freezing point were measured. The results obtained through DSC tests were found to be very close to those of the experimental results, thus the experimental results are in good agreement with analytical results. It can be concluded that a PCM without supercooling can be used as a latent heat storage material for heating and cooling and space air-conditioning applications in the thermal comfort range of suitable temperature.

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