The role of chemical additives to the phase change process of CaCl$_2$.6H$_2$O to optimize its performance as latent heat energy storage system

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Abstract. CaCl$_2$.6H$_2$O is one of salt hydrate based phase change material (PCM) which is suitable for room air-temperature stabilizer because it has the melting temperature just above the human comfort zone temperature ($T_m$ ~ 29 °C) and a relatively large heat enthalpy ($\Delta H$ ~ 190 kJ/kg). This paper reports the role of the type of chemical additives to PCM CaCl$_2$.6H$_2$O to the phase change process throughout the solidification process or heat release in order to optimize its performance as latent heat energy storage system. In this research we used several kinds of chemical additive, namely SrCl$_2$.6H$_2$O (1.0 wt%), BaCO$_3$ (0.5 wt%), and K$_2$CO$_3$ (0.5 wt%). In terms of its latent time for phase change process the order the effectiveness of those chemical additives are reduced from SrCl$_2$.6H$_2$O, BaCO$_3$and K$_2$CO$_3$. We found that this is also related to their role in suppression supercooling and phase separation effects which occurs during crystallization process of CaCl$_2$.6H$_2$O.

1. Introduction

Thermal energy storage (TES) technologies can reduce the peak electric power loads in buildings, and utilize benefits of waste heat recovery and renewable energy [1]. Phase change materials (PCM) as the latent heat energy storage offer more advantage compared with those of sensible heat energy such as water and bricks because it can store relatively large heat enthalpy at temperature around its phase change. One of potential candidate of inorganic PCM for this application is Calcium Chloride Hexahydrate, CaCl$_2$.6H$_2$O, with the melting temperature of around 29°C, relatively high heat enthalpy of about 190 kJ/kg, relatively good thermal conductivity of $\kappa = 0.58$ W/m·K, and relatively high density of $\rho = 1710$ kg/m$^3$[2-4].

Understanding crystallization and melting processes of CaCl$_2$.6H$_2$O is a fundamental key for its research and technology development [1,2]. Hence, heat is stored in the PCM by melting process, and recovered during its freezing. According to the thermodynamics, the freezing or solidification does not occur spontaneously due to the fact that it involves the decrease of the entropy of the system [5]. In particular for PCM CaCl$_2$.6H$_2$O, one has to overcome two general problems of supercooling and phase separation effects [2-4]. We note that the crystallization process involves several steps: an induction period, a crystal growth phase, and a period of recrystallization or crystal regrowth [6].
Several chemical additives at certain amount have been recognized effective to prevent the supercooling and phase separation effect of CaCl₂·6H₂O [7]. According to the similarity in the crystal structure and lattice parameters of the CaCl₂·6H₂O and additive, the additive are classified as isomorphous nucleator and non-isostructural nucleator. Among them we have shown in our previous paper that SrCl₂·6H₂O (1.0 wt%) as isomorphous nucleators to CaCl₂·6H₂O effectively suppress the supercooling and phase separation effect, followed by non-isostructural nucleators of BaCO₃ (0.5 wt%) and K₂CO₃ (0.5 wt%) [8]. The phase change process of CaCl₂·6H₂O can be assessed from its time-dependent temperature. In this paper we present the effectiveness of these particular additives in terms of its nucleation time and latent time related to phase change process. We also compare our results with the suppression of supercooling and phase separation effect due to type of chemical additives. It is worth mention that this study is particularly useful to ensure the performance of PCM as latent heat energy storage system.

2. Methods
Salt hydrate CaCl₂·6H₂O is provided from Sigma Aldrich Company with purity 98%. A sample of about 20 grams was prepared in the chemical reaction tube made from glass and a certain amount of the test nucleator was added. They are 1.0 wt% SrCl₂·6H₂O, 0.5 wt% BaCO₃ and 0.5 wt% K₂CO₃. The sample was heated to temperature just above its melting point, thoroughly mixed, and allowed to cool to room temperature. The crystal growth process of the sample were evaluated by recording the time-temperature record, monitored by Arduino microcontroller board using LM35 temperature sensor immersed into the liquid part of the sample with sensitivity of the sensor was configured to have the value of ±0.17°C. The data are collected through Meguno Link Pro software using time interval of 5 second for total measurement time of about 24 hours and the overall measurement system is connected to the PC. The experiments are repeated several times to obtain the cycling stability data of each sample. Figure 1 show the experimental apparatus consist of Arduino microcontroller, LM35 temperature sensor, and PCM samples in the reaction tube.

![Figure 1](image.png)

**Figure 1.** The experimental apparatus consist of: (a) Arduino microcontroller, (b) LM35 temperature sensor, and (c) PCM samples in the reaction tube.

3. Results and discussion
The graphs for crystallization process of pure CaCl₂·6H₂O and with certain kind of additives, namely: 1.0 wt% SrCl₂·6H₂O, 0.5 wt% BaCO₃, and 0.5 wt% K₂CO₃ and are shown in figure 2 (a) for the data taken at 6th of cycle. We compare the data with typical crystallization curve, figure 2(b), that show several parameters, such as supercooling temperature (Tₛ), crystallization temperature (T_c), nucleation time (tₙ), and liquid-solid phase change process (tₚ) [6].
From this figure, the crystallization curves of CaCl$_2\cdot$6H$_2$O show the minimum temperature or deep (point A) signifying the supercooling of the liquid and the barrier that have to be overcome during the crystallization process. The crystal growth process is starting from this point through the formation of nucleus. These nucleuses will start to grow by forming a new surface between liquid and crystal. This process requires a large amount of energy (Gibbs energy) and also the release of heat, causing the increase of the temperature (point B). The difference in temperature between these two A and B points signifying the supercooling temperature ($T_s$). The nucleus growth rate can be determined from the value of induction or nucleation time ($t_i$), i.e. the time required for the growth of nucleus. The crystal growth process actually occurs from point B to point C, namely during the latent time ($t_n$), and ideally occurs at a constant temperature, namely the crystallization temperature ($T_c$). The process is then continued by a redistribution process to modify the shape and size of the crystals to become more perfect (point D). The equilibrium state condition of this process was achieved when the crystal temperature reaches point E.

From the experimental data one can see that the effect of additives generally reduce the subcooling of CaCl$_2\cdot$6H$_2$O [7,8]. For further evaluation of nucleation time and latent time, we evaluate the A, B, C and D points from each of time-temperature dependent data, and figure 3 give the illustration of this procedure. Table 1 gives the summary of crystallization experiment of CaCl$_2\cdot$6H$_2$O for the further analysis, namely the average nucleation time, the average latent time, and the average supercooling temperature taken from about 19 cycling data. Shown also in this table the supercooling temperature obtained from our previous results, i.e. using the value of sensitivity sensor of ±0.5°C [8].
Figure 3. The illustration for determination of phase change process (points A, B, C, D and E) of CaCl$_2$.6H$_2$O with additive 0.5 wt% K$_2$CO$_3$.

Table 1. The average induction time, latent time and supercooling of CaCl$_2$.6H$_2$O without and with various type and amount of chemical additive.

| Additive     | Induction time, $t_i$ (minutes) | Latent time, $t_n$ (minutes) | Supercooling ($^\circ$C) | Supercooling $^a$ ($^\circ$C) |
|--------------|---------------------------------|------------------------------|--------------------------|-------------------------------|
| 1.0 wt% SrCl$_2$.6H$_2$O | 19                             | 112                          | 0.3                      | -                             |
| 0.5 wt% BaCO$_3$ | 50                             | 148                          | 0.95                     | 0.59                          |
| 0.5 wt% K$_2$CO$_3$ | 107                            | 247                          | 0.92                     | 1.07                          |
| None         | 178                            | 238                          | 1.8                      | 4.59                          |

$^a$) The data taken from Ref. [8] using the value of sensitivity sensor of $\pm0.5^\circ$C

From this table one can see that the chemical additive generally have the role to reduce the induction time, the latent time and the supercooling temperature, although the latent time of CaCl$_2$.6H$_2$O added with 0.5 wt% K$_2$CO$_3$ was a little longer than the CaCl$_2$.6H$_2$O without additive. We note in this connection that the role of chemical additive is to increase the speed rate of crystallization and to reduce the crystallization barrier. These favorable conditions are needed for the optimal application of CaCl$_2$.6H$_2$O as the latent heat energy storage, due to the fact that high speed rate during the crystallization can reduce the time lag of PCM in response to the air environment change and high supercooling can totally prevent the heat release.

4. Summary
We have shown in this paper that certain type and amount of the chemical nucleator additive have the impact to the crystallization process of PCM CaCl$_2$.6H$_2$O, namely 1.0 wt% SrCl$_2$.6H$_2$O, 0.5 wt% BaCO$_3$ and 0.5 wt% K$_2$CO$_3$. These chemical nucleators generally have the role to reduce the induction time, the latent time and the supercooling temperature. In terms of that parameters, the effectivity of those chemical additives are reduced in order from SrCl$_2$.6H$_2$O, BaCO$_3$ and K$_2$CO$_3$. 
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