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PERFORMANCE OPTIMIZATION OF INORGANIC SALT HYDRATE PCMs FOR THERMAL ENERGY STORAGE IN TROPICAL APPLICATIONS

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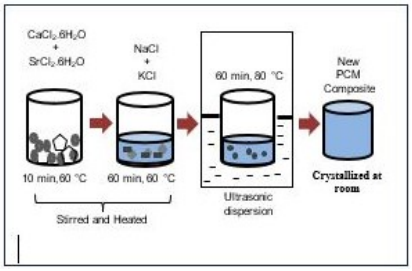
Graphical abstract



Abstract

The phase change materials (PCMs) for thermal energy storage (TES) are becoming more and more popular as a result of the growing demand for effective energy storage solutions. The use of inorganic salt hydrates, which are recognized for their high thermal energy storage and desirable thermophysical properties, has the potential to enhance TES performance. This study explores the thermophysical properties and phase transition behavior of selected inorganic salt hydrates, investigating their suitability for energy storage. Innovative synthesis methods, including the direct mixing of molten salts and the combination of multiple salt hydrates, were employed to address issues such as supercooling and phase segregation. A novel eutectic salt hydrate-based mixture was formulated by integrating thickening agents, resulting in improved performance. The study utilized aqueous solutions of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$), strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$), potassium chloride (KCl), as well sodium chloride (NaCl), with thermophysical properties analyzed via Differential Scanning Calorimetry (DSC). The best mixture, containing 96.0 wt.% $CaCl_2 \cdot 6H_2O$, 1.5 wt.% $SrCl_2 \cdot 6H_2O$, 2.0 wt.% KCl, and 0.5 wt.% NaCl, demonstrated a 4.65% increase in latent heat capacity. Additionally, the mixture displayed stable melting onset temperatures, making it ideal for TES applications in tropical climates like Malaysia. The effectiveness of the optimized salt hydrate composition is highlighted in this study, marking a significant sustainable advancement in storing energy.

Keywords: Thermal Energy Storage (TES), Salt Hydrates, Phase Change Materials (PCMs), and Sustainable

Abstrak

Bahan perubahan fasa (Phase Change Materials, PCMs) untuk penyimpanan tenaga haba (Thermal Energy Storage, TES) semakin mendapat perhatian disebabkan oleh permintaan yang meningkat terhadap penyelesaian penyimpanan tenaga yang berkesan. Penggunaan garam hidrat tak organik, yang dikenali kerana keupayaan penyimpanan tenaga haba yang tinggi dan sifat termofizikal yang unggul, berpotensi untuk meningkatkan prestasi TES. Kajian ini meneliti sifat termofizikal dan tingkah laku perubahan fasa bagi beberapa garam hidrat tak organik terpilih serta kesesuaiannya untuk aplikasi penyimpanan tenaga. Kaedah sintesis inovatif, termasuk pencampuran langsung garam cair dan kombinasi beberapa garam hidrat, telah digunakan untuk

menangani isu seperti penyejukan berlebihan (supercooling) dan pemisahan fasa. Campuran garam hidrat eutektik baharu diformulasikan dengan menambah agen pemekat, menghasilkan prestasi yang lebih baik. Kajian ini menggunakan larutan akueus kalsium klorida heksahidrat ($CaCl_2 \cdot 6H_2O$), strontium klorida heksahidrat ($SrCl_2 \cdot 6H_2O$), kalium klorida (KCl), dan natrium klorida (NaCl), dengan sifat termofizikalnya dianalisis melalui Kalorimetri Pengimbasan Pembezaan (Differential Scanning Calorimetry, DSC). Campuran optimum yang mengandungi 96.0 wt.% $CaCl_2 \cdot 6H_2O$, 1.5 wt.% $SrCl_2 \cdot 6H_2O$, 2.0 wt.% KCl, dan 0.5 wt.% NaCl menunjukkan peningkatan kapasiti haba pendam sebanyak 4.65%. Selain itu, campuran ini mempamerkan suhu mula lebur yang stabil, menjadikannya sesuai untuk aplikasi TES di iklim tropika seperti Malaysia. Keberkesanan komposisi garam hidrat yang dioptimumkan ini diserlahkan dalam kajian ini, menandakan kemajuan mampan yang signifikan dalam penyimpanan tenaga.

Kata kunci: Penyimpanan Tenaga Haba (TES), Garam Hidrat, Bahan Perubahan Fasa (PCMs), dan Kelestarian

1.0 INTRODUCTION

Phase change materials (PCMs) have great potential for storing and releasing a large amount of thermal energy during phase change between solid and liquid states. This characteristic enables them to be used as energy storage devices with solar energy, building temperature control and electronic device cooling applications (including the development of alternative powered vehicles). Among various PCMs, inorganic salt hydrates have emerged as promising candidates due to their high latent heat, availability, and relatively low cost [1], [2]. The use of $CaCl_2 \cdot 6H_2O$ as a base PCM is attractive because of its favorable thermophysical properties and affordability. However, phase segregation and supercooling can hinder practical applications for using it. In response to these problems different nucleating agents and thickening agents have been studied [3]–[5].

The PCMs are generally classified into different groups based on the composition of their material. As shown in Table 1, the primary types of PCMs include organic, inorganic, and eutectic [6]–[8]. In particular, inorganic salt hydrates stand out for their excellent latent heat storage capacity, affordability, and non-flammable nature [9]–[12].

Table 1 PCM classification

Features	Organic	Inorganic	Eutectic
Corrosive	No	Yes	No
Supercooling	No	Yes	No
High heat of fusion	No	Yes	Yes
Thermal conductivity	Low	Good	Moderate
High changes in volume during phase transition	Yes	No	No
Cost	High	Low	Moderate

Many researchers have explored compounded inorganic salt hydrates to optimize phase change temperatures and improve cold storage efficiency. Lovera *et al*. [13] focused on developing, characterizing, and modifying new PCMs that are based on salt hydrates. Their experiments on eutectic mixtures revealed excellent thermal properties, which made these materials perfect for applications such as PCMs and simulating air conditioning systems and refrigeration for both commercial and residential settings. Similarly, Simon *et al*. [1], [2] a prior research investigated the use of an inorganic eutectic PCM for temperature management in buildings with roof slab, using a test room built at site. Xiang *et al*. [14], [15] identified inorganic salt hydrates as the most efficient thermal latent heat storage material for passive solar systems.

Recent research has focused on modifying PCM compositions with additives such as nucleating agents [16]–[19], thickening agents [6], [20], [21] encapsulation [22], [23] and others to reduce supercooling and prevent phase segregation. Tyagi *et al*. [30] demonstrated that adjusting the pH and adding nucleating agents could effectively reduce supercooling. For example, a study by [18] found that 1.0 wt% $Sr(OH)_2 \cdot 8H_2O$ effectively reduced supercooling in $CaCl_2 \cdot 6H_2O$, while $Ba(OH)_2$ balanced suppression of crystallization with minimal impact on storage capacity.

Thakkar *et al*. [24] found that the thermal storage properties of $CaCl_2 \cdot 6H_2O$ can be improved significantly when being mixed with a filler like KCl in small quantity for increasing phase change enthalpy as well as energy transfer. In an additional attempt to hasten thermal responsiveness, Dash *et al*. [25] manufactured a new type of hybrid PCM combined with graphite and salt hydrate-based phase change materials. Meanwhile, Wang *et al*. In the literature, Emmel *et al*. [26] investigated the cycling stability of a microencapsulated CaCl2–based PCM system.

Inspired by those previous works, the current research seeks to extend knowledge in the area of salt hydrate-based mixtures as PCM by developing a novel eutectic mixture and investigating its thermodynamic

performance operating within different endorsed thermal modes. The formulation couples $SrCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ with KCl and NaCl to increase latent heat capacity, reduce supercooling, and increase phase stability.

2.0 METHODOLOGY

2.1 Materials and Preparation of Eutectic Salt Hydrate-Based Mixtures

In this work, a phase change material (PCM) system containing partially potassium sulphate and calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) was studied for its supercooling behavior, phase transition temperature and thermal conductivity. The materials were selected due to their favorable thermophysical properties and affordability, making them practical for large-scale thermal energy storage (TES) applications.

To improve the stability of the PCM, strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$) was added as a nucleating agent [24], and for thickening agent potassium chloride (KCl) [27][28] and sodium chloride (NaCl) were incorporated to enhance viscosity and reduce segregation. The materials were purchased from Biotek Abadi Sdn Bhd (Table 2).

Table 2 Thermophysical properties of materials used

Salt Hydrates	Melting Temp. (°C)	Latent Heat (J/g)
$CaCl_2.6H_2O$	30.0	174
$SrCl_2.6H_2O$	115.0	-
NaCl	801.0	0.86
KCl	776.0	0.695

Direct mixing of molten salts with salt hydrates was deliberately avoided due to the chemical risks involved. Molten salts such as sodium chloride (NaCl) and potassium chloride (KCl) have very high melting points (801 °C and 776 °C, respectively). At such elevated temperatures salt hydrates like $CaCl_2 \cdot 6H_2O$ undergo thermal decomposition, releasing their water of hydration and resulting in incongruent melting and phase separation. This leads to significant degradation of the PCM's thermophysical stability. Therefore, a low temperature preparation strategy was employed to maintain the structural integrity of the hydrate components and ensure homogeneous dispersion.

The preparation process was carried out in two steps. First, a surfactant was mixed with the base PCM ($CaCl_2 \cdot 6H_2O$) and the nucleating agent ($SrCl_2 \cdot 6H_2O$), stirred at 60°C for 10 minutes. Then, NaCl and KCl were added, and the solution was further stirred at 80°C for 60 minutes. Finally, ultrasonic vibrations were applied for 60 minutes at 40 kHz to improve the dispersion of the mixture and reduce agglomeration, promoting a more stable PCM composition.

This preparation method allowed for uniform mixing and phase stability without subjecting the materials to excessive thermal stress. A schematic of the process is shown in Figure 1.

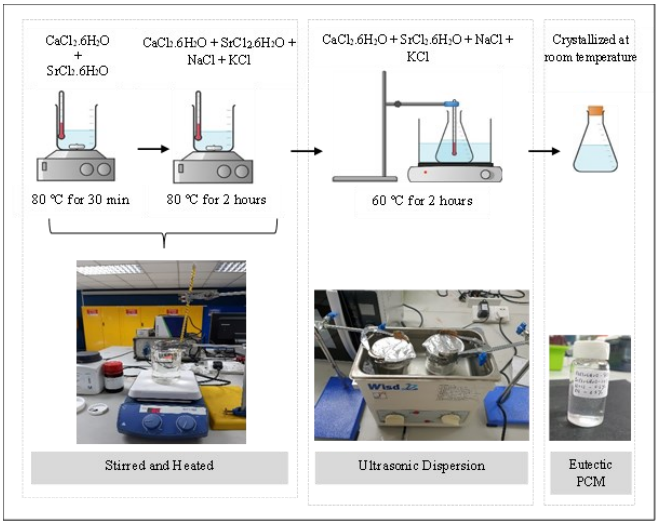


Figure 1 Schematic preparation of inorganic eutectic PCM sample

2.2 Experimental Setup

Six samples of eutectic mixtures were prepared with varying compositions, as described in Table 3, to evaluate their phase transition behavior and thermophysical properties. Each sample was precisely weighed using an analytical balance to ensure accurate proportions, with the total weight of each sample maintained at approximately 5 grams. Measurement was performed using a TA Instruments Q20 Differential Scanning Calorimeter unit as shown in Figure 2.

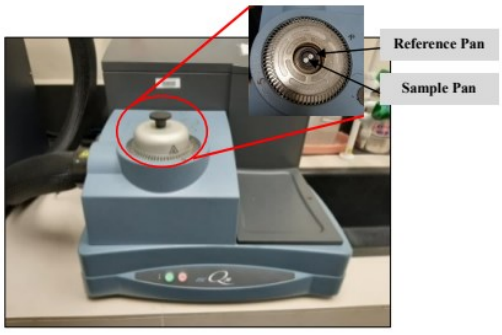


Figure 2 Differential scanning calorimeter (DSC) model Q20, with inset of sample and reference pans

Thermal behavior was assessed by heating samples from -10 to 80°C at a constant rate of 7°C/min using the Differential Scanning Calorimeter (DSC Q-20; PerkinElmer) in a nitrogen flow of 30 ml/min. This heating and cooling cycles were repeated up to 10 cycles, waiting for the sample in each temperature for

2 hours to ensure thermal equilibrium was achieved. The sample was heated during the controlled temperature heating program and the heat was cooled by allowing the system to cool in the calorimeter.

Table 3 outlines the composition of the various PCM mixtures tested. The experimental procedure followed a systematic approach to optimize the mixture and improve its latent heat storage capacity.

Table 3 Composition of the modified PCM

Mixture A (Control)	Weight ratio (%)	Mixture B	Weight ratio (%)	Mixture C	Weight ratio (%)
$CaCl_2.6H_2O$	100	$CaCl_2.6H_2O$	96.5	$CaCl_2.6H_2O$	96.5
$Ba(OH)_2.8H_2O$	-	$Ba(OH)_2.8H_2O$	1.0	$SrCl_2.6H_2O$	1.0
KCl	-	KCl	2.0	KCl	2.0
NaCl	-	NaCl	0.5	NaCl	0.5
Mixture D	**Weight ratio (%)**	**Mixture E**	**Weight ratio (%)**	**Mixture F**	**Weight ratio (%)**
$CaCl_2.6H_2O$	97.0	$CaCl_2.6H_2O$	98.0	$CaCl_2.6H_2O$	96.0
$SrCl_2.6H_2O$	1.5	$SrCl_2.6H_2O$	1.5	$SrCl_2.6H_2O$	1.5
KCl	0.5	KCl	0.25	KCl	2.0
NaCl	1.0	NaCl	0.25	NaCl	0.5

The varying percentages of $CaCl_2 \cdot 6H_2O$ in the different mixtures (ranging from 96% to 100%) were selected to evaluate its effect on the thermal performance and phase stability of the PCM. Higher concentrations of $CaCl_2 \cdot 6H_2O$ were used in mixtures where the primary focus was to maintain high latent heat capacity and ensure optimal thermal storage efficiency. In contrast, the moderate decrease in $CaCl_2 \cdot 6H_2O$ in $SrCl_2 \cdot 6H_2O$, NaCl, and KCl-added mixtures was for enhanced supercooling inhibition and enhanced phase stability by nucleating agents and thickening agents. Small amounts of the sub-components (about 1% to 2%) were added to evaluate their ability to reduce supercooling and stabilize phase transition behavior while maintaining the latent heat capacity with minimal compromise.

2.3 Analysis Method

Thermodynamic properties of phase change materials (PCMs) were determined by a differential scanning calorimeter (DSC Q-20). DSC analyses were conducted at 7 °C/min with nitrogen flow rate of 30 ml/min. The experiments were performed using 5 g samples cycled between -10°C and 80°C to test the landfill earthworm's waxy product, PCM, and studies measuring its latent heat of fusion with increasing cycle number (DSC melting curves from the supernatant liquid after 10 cycles, then after 50 cycles). The phase transition of a specimen (including onset temperature, peak temperature and latent heat) during each cycle can be derived from the measurement of latency or stability.

3.0 RESULTS AND DISCUSSION

3.1 Behavior During Phase Transitions

DSC analysis was conducted on the various mixtures of PCMs to examine their phase transition behaviour. Figure 2 presents the heating curve for calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) across 10 thermal cycles. With each cycle, $CaCl_2 \cdot 6H_2O$ progressively lost water, forming lower hydrates, which led to incongruent melting. The presence of $CaCl_2 \cdot 4H_2O$ was indicated by the onset of a peak at 48°C during the 10th cycle. So too did its latent heat of melting decrease as a function of the number of cycles. Table 4 presents the onset and peak melting temperatures, as well as the latent heat capacity for a maximum of ten cycles.

The temperatures are utilized for confirming and validating the melting/freezing points, with full solidification/melting being observed. The latent heat of phase transition is determined using (1) [29][30].

$$\Delta H = \frac{A}{M} \quad (1)$$

Where A denotes area under the DSC peak (J), M signifies sample mass (g), and ΔH stands for latent heat (J/g). The latent heat associated with the phase change is connected to the specific heat capacity, with all other conditions kept constant.

The results highlight the material's instability over multiple thermal cycles, necessitating stabilization measures to prevent incongruent melting and phase separation.

3.2 Comparison of Behaviour

The DSC thermograms of six samples for three cycles are shown in Figure 3 to Figure 8. All DSC measurements were performed in triplicate to ensure repeatability and consistency. The reported values of melting temperature, freezing temperature, and latent heat represent the average of three independent measurements. The measurement uncertainty was estimated based on instrument calibration standards and repeatability errors. The temperature measurement uncertainty was ±0.2 °C, while the latent heat measurement uncertainty was within ±5%. These uncertainties were within the acceptable range for PCM characterization and did not significantly affect the interpretation of the results.

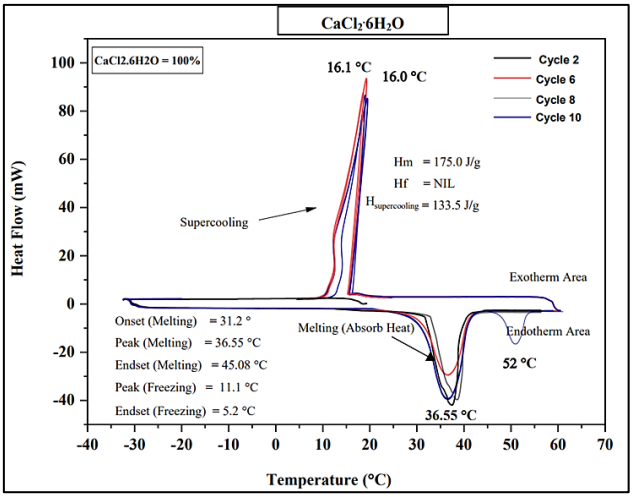


Figure 3 DSC curve depicting the thermal behavior of $CaCl_2 \cdot 6H_2O$ over the initial 10 cycles

Figure demonstrates that as the number of heating-cooling cycles increases, $CaCl_2 \cdot 6H_2O$ gradually loses water, forming lower hydrates, resulting in incongruent melting. The presence of $CaCl_2 \cdot 4H_2O$ is indicated by a peak onset temperature of 48 °C observed during the 10th cycle. The latent heat of melting decreases as the number of cycles increases. Table 4 includes data on onset and peak melting temperatures, as well as latent heat capacity for up to ten cycles. These results indicate that $CaCl_2 \cdot 6H_2O$ is vulnerable to instability, highlighting the need for stabilization to prevent incongruent melting and phase separation.

The reduction in latent heat of fusion during repeated thermal cycles, observed in Mixture B and Mixture C, is due to the progressive release of water molecules from the $CaCl_2 \cdot 6H_2O$ compound. This desiccation results in the creation of less hydrated forms like $CaCl_2 \cdot 4H_2O$, which have a decreased capacity for storing energy. The repeated heating and cooling cycles accelerate this process, causing irreversible structural changes and phase segregation. Moreover, partial phase separation and insufficient rehydration reduce the consistency and magnitude of the latent heat during each cycle. These phenomena explain the downward trend in thermal energy storage performance over successive cycles.

Table 4 The melting point temperature (Tm), peak temperature (Tp) and latent heat capacity for $CaCl_2 \cdot 6H_2O$ over 10 cycles

Cycle No.	T_m Onset (°C)	T_p Peak (°C)	T_f Onset (°C)	T_f Peak (°C)	H_m (J/g)	H_f (J/g)
2	30.2	35.1	15.1	16.0	175	133.1
6	30.2	35.2	15.2	16.0	173	133.1
8	26.8	36.55	15.2	16.1	169	133.4
10	26.2	36.55	15.5	16.1	165	133.5

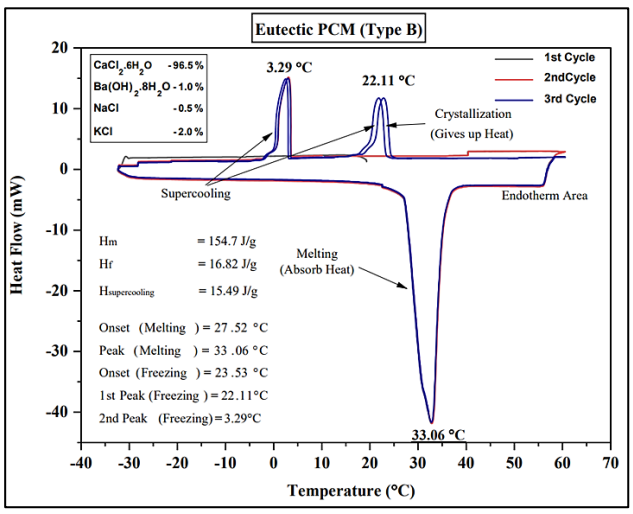
* H_m = Melting heat capacity
H_f = Freezing heat capacity

Mixture B (Figure 4a), which contained $Ba(OH)_2 \cdot 8H_2O$ as the nucleating agent, exhibited pronounced supercooling and moderate latent heat capacity. Mixture C (Figure 4b), which used $SrCl_2 \cdot 6H_2O$ instead, showed more consistent freezing profiles and improved nucleation behavior, although it resulted in a slightly lower melting enthalpy. The melting temperature for Mixture B was recorded at 27.52°C with a latent heat capacity of 154.7 J/g. This result aligned closely with [21]. Multiple exothermic peaks were observed during the freezing process, indicative of supercooling.

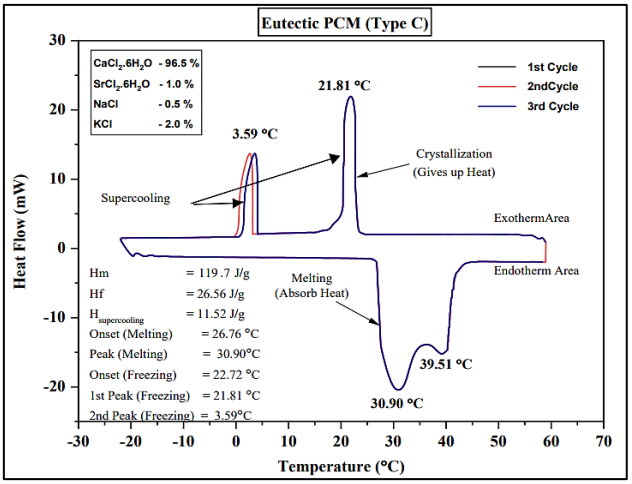
Mixture C, which replaced $Ba(OH)_2 \cdot 8H_2O$ with $SrCl_2 \cdot 6H_2O$, exhibited similar melting and freezing temperatures. The use of $SrCl_2 \cdot 6H_2O$ was effective in reducing supercooling, resulting in a freezing enthalpy value 36.7% higher than that of Mixture B. However, Mixture C displayed a slightly lower melting enthalpy, highlighting the need for further optimization of the nucleating agent ratio.

The comparative analysis of Figure 4 reveals that Mixture B experiences pronounced supercooling, as seen from the multiple exothermic peaks during the freezing phase, and also shows moderate latent heat capacity. In contrast, Mixture C exhibits a more consistent freezing profile with fewer exothermic fluctuations, indicating enhanced phase transition stability. The presence of $SrCl_2 \cdot 6H_2O$ in Mixture C significantly improves nucleation behavior, thereby suppressing supercooling more effectively than $Ba(OH)_2 \cdot 8H_2O$ in Mixture B. However, this improvement is accompanied by a slight decrease in melting enthalpy, indicating a trade-off between thermal stability and energy storage capacity.

In conclusion, $SrCl_2 \cdot 6H_2O$ serves as a more effective nucleating agent than $Ba(OH)_2 \cdot 8H_2O$ in reducing supercooling, making Mixture C more suitable for practical TES applications where thermal consistency is prioritized over maximum heat storage.



(a)

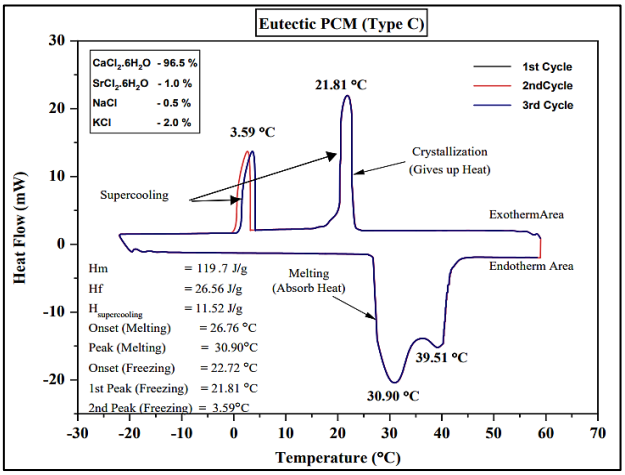


(b)

Figure 4 DSC thermogram. (a) Mixture B – showing decreased latent heat due to phase instability; (b) Mixture C – improved supercooling suppression but also exhibiting heat capacity loss over cycles.

3.3 Optimization of PCM Composition

Figure 5 shows the DSC thermogram for Mixture C, D, E, and F to investigate the optimize PCM composition.



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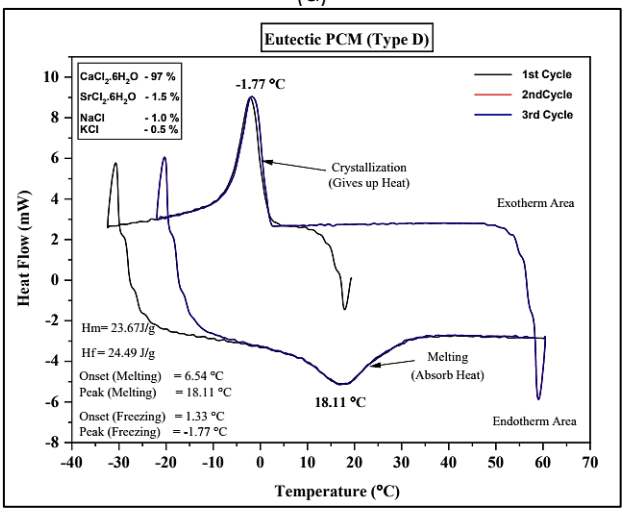

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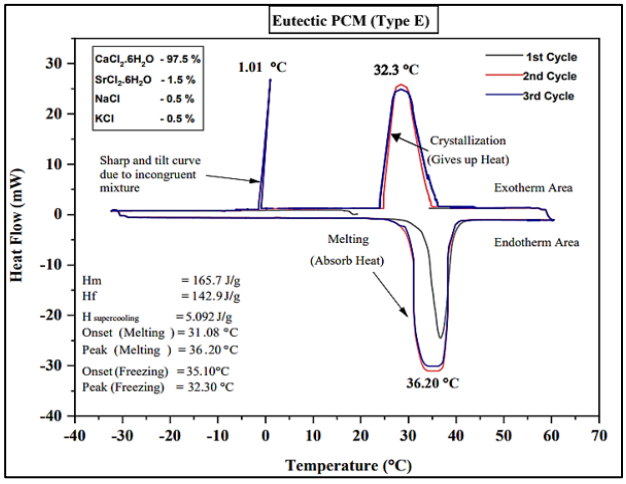

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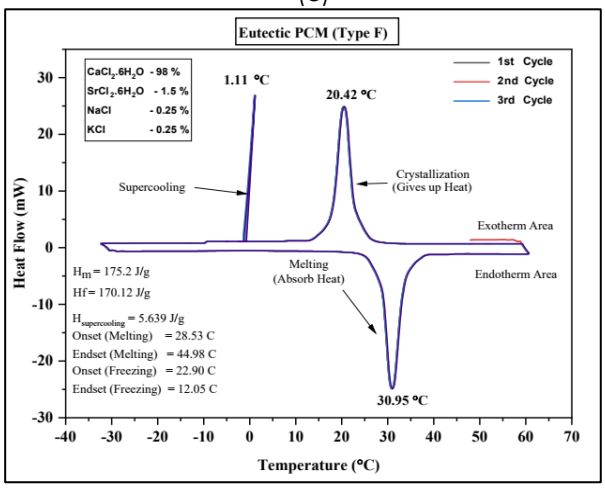

(d)

Figure 5 DSC thermogram. (a) Mixture C; (b) Mixture D; (c) Mixture E; and (d) Mixture F

Figure 5(a) – (d) and Table 5 present DSC thermograms and thermophysical properties of Mixtures C to F.

Table 5 Thermophysical properties summary of inorganic eutectic PCM mixtures

Mixture	Melting Temperature, T_m (°C)		Latent Heat, ΔH_m (J/g)	Freezing Temperature, T_f (°C)		Latent Heat, ΔH_f (J/g)
	Onset	Peak		Onset	Peak	
A	31.2	36.5	175.0	16.1	11.1	133.5
B	27.5	33.1	154.7	23.5	22.1	16.8
C	26.8	30.9	119.7	22.7	21.9	26.6
D	6.54	18.1	23.7	1.33	-1.77	24.5
E	31.1	36.2	165.7	35.1	32.3	142.9
F	28.5	44.9	175.2	12.0	20.4	170.1

Mixture F displayed the highest latent heat capacity and reduced supercooling. The narrow melting peak observed for Mixture F at 30.95°C, combined with its high latent heat capacity and reduced supercooling, indicates eutectic behavior. This optimized composition demonstrates a stable phase transition compared to single component hydrates, confirming that the synergistic effect of the salt hydrate mixture provides enhanced thermophysical performance.

The endothermic curve suggests an exothermic reaction attributed to crystallization [31]. In a differential scanning calorimetry (DSC) curve, endothermic peaks typically correspond to the melting phase, where the material absorbs heat to transition from solid to liquid. In contrast, exothermic peaks indicate crystallization or freezing, where heat is released as the material transitions from liquid to solid. Thus, crystallization is signified by an exothermic peak, not an endothermic one.

The shape, position, and area under these peaks offer valuable information about the material's melting point, freezing behavior, and latent heat capacity. Energy is required in this process to surpass the intermolecular forces that hold the solid together, leading to a noticeable endothermic peak. The position and characteristics of this peak on a DSC curve offer crucial insights into the material, such as its melting point and enthalpy [27][28]. The temperature where the endothermic peak is observed signals the melting point, with the peak's area reflecting the enthalpy of fusion - the energy needed to melt the sample. Enthalpy, determined by integrating the heat flow data, is quantified following ASTM E793 [32]. This measurement offers important information regarding the material's purity and thermal stability.

3.4 Reducing Supercooling in $CaCl_2 \cdot 6H_2O$

Supercooling poses a significant challenge commonly faced by inorganic PCMs, and its mitigation is crucial for optimizing latent heat energy storage systems. Suppressing supercooling is vital as it directly impacts the solidification process, influencing the thermal energy release and heat transfer efficiency. The term "supercooling peak" describes an exothermic peak observed in certain materials during the cooling or solidification process, visible as a peak on the DSC curve [33]. In a DSC analysis, when a material experience supercooling during cooling (from a higher temperature to a lower one), it can result in the observation of a supercooling peak. This peak appears as a sharp exothermic spike on the DSC curve when the material eventually crystallizes or solidifies releasing the latent heat of fusion associated with the transition from liquid to solid state. This heat release is what produces the exothermic peak [34].

Rahman *et al*. [35] identified two methods for determining the supercooling value: (i) calculating the temperature difference ($T = T_m - T_f$) based on the peak temperatures of the melting and freezing curves, and (ii) measuring the supercooling value using the onset temperatures of both the endothermic and exothermic curves. The authors suggest that the first method provides a more accurate assessment of supercooling. This is because peaks temperatures reflect the most significant thermal events and are less susceptible to baseline noise, offering higher repeatability in practical DSC measurements. Refer to Figure 5 for a detailed explanation.

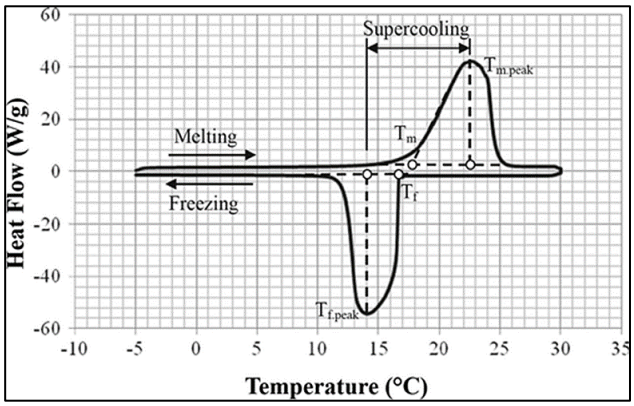

Figure 6 Supercooling degree identifying method based on the melting and freezing curves from the DSC test [35].

For the calcium-based solution, strontium chloride hexahydrate (SrCl2·6H2O) was selected as the nucleating agent. According to Guo *et al*. [36] and Thakkar *et al*. [24] the most effective nucleating agents for calcium-based solutions typically fall within a mass range of 0.5% to 2%. This study investigated the influence of SrCl2·6H2O concentration on the level of supercooling in the calcium-based solution. The supercooling degree was determined by subtracting the peak melting temperature from the peak crystallization (freezing) temperature. ASTM D3418 (2008) provides guidelines for calculating enthalpy, melting temperature, and crystallization temperature. It suggests that the freezing and peak melting temperatures should differ by no more than 20%. To further explore this, $SrCl_2 \cdot 6H_2O$ was added in concentrations of 1.0 wt.% and 1.5 wt.% to the modified $CaCl_2 \cdot 6H_2O$. The impact of adding $SrCl_2 \cdot 6H_2O$ at various weight percentages was analyzed through the DSC curves presented in Figures 2 to 7. A comprehensive summary of the peak melting temperature, peak freezing temperature, and total supercooling degree is provided in Table 6.

As presented in Table 6, the supercooling level of the calcium-based solution with 1.5% by mass of $SrCl_2 \cdot 6H_2O$ added was determined to be 3.90°C and 3.15°C in Mixtures E and F, respectively. Increasing the mass of $SrCl_2 \cdot 6H_2O$ while simultaneously reducing the mass of NaCl and KCl led to a notable decrease in the supercooling degree for Mixtures C, E, and F, with values ranging between 3°C and 9°C. This occurs because $SrCl_2 \cdot 6H_2O$ provides abundant nucleation sites that promote early and uniform crystal formation during freezing, thereby reducing the extend of

supercooling. In contrast, NaCl and KCl, primarily act as thickening agents and may inhibit efficient crystallization at higher concentrations by increasing viscosity or disrupting molecular alignment.

Table 6 Summary of supercooling degree

Mix.	T_m – Peak (°C)	T_f – Peak (°C)	$\Delta_s = T_m - T_f$ (°C)
A	36.55	16.10	20.45
B	33.06	22.11	10.95
C	30.90	21.81	9.09
D	18.11	-1.77	19.88
E	36.20	32.30	3.90
F	30.95	27.80	3.15

* T_m = Melting temperature
T_f = Freezing temperature
Δ_s = Degree of supercooling

A maximum reduction of 84.5% was observed, indicating that the supercooling degree decreases as the volume of $SrCl_2 \cdot 6H_2O$ increases and the amount of NaCl and KCl decreases in equal proportions. For comparison, Mixture A, composed of pure $CaCl_2 \cdot 6H_2O$, exhibited a supercooling degree of 20.45 °C and a freezing temperature of 16.10 °C. According to the literature Yan *et al*. [37] and Li *et al*. [38] the supercooling degree for pure $CaCl_2 \cdot 6H_2O$ typically falls between 14 °C and 20 °C, aligning with the results obtained in this study. The lowest supercooling degree, 3.15 °C, was recorded for the F-type PCM mixture, followed by the E-type PCM mixture with a supercooling degree of 3.90 °C. This lowest supercooling degree, together with the stable melting point of 30.95°C, further supports the classification of Mixture F as a eutectic PCM. The mixture achieves thermal stability and energy storage efficiency that are characteristic of eutectic formulations, justifying the use of the term 'eutectic' in describing this optimized composition. These results demonstrate that $SrCl_2 \cdot 6H_2O$ serves as an effective nucleating agent for reducing supercooling in calcium-based solutions. A supercooling degree below 10 °C is considered preferable, and therefore, Mixtures E and F shall be investigated further for thermal stability since they have potential for eutectic PCM production. These mixtures show potential for use in the production of eutectic PCMs as optimal heat-absorbing materials.

3.5 Thermal Stability Performance of Designed Eutectic PCM

The thermal stability of phase change materials (PCMs) is critical for their engineering applications. It is essential for PCMs to exhibit minimal variations after undergoing numerous thermal cycles to ensure their long-term viability as latent heat storage materials. When salt hydrates are heated to their melting point, they become only partially soluble in their hydration water, leading to phase separation. As heat-cooling cycles are repeated, salt deposition increases, causing a progressive reduction in the material's heat storage capacity. Phase separation significantly impacts the energy storage density of PCMs over multiple cycles, making it the primary factor influencing their thermal reliability [39][33].

To simulate the extended use of PCM in building envelope applications, Mixtures E and F underwent 180 repeated melting and freezing cycles using Differential Scanning Calorimetry (DSC). This method emulates approximately six months of real-world daily thermal cycling, with each cycle representing a day of exposure to heating and cooling conditions within a building environment. Each DSC cycle lasted 120 minutes, and the samples' thermal stability was assessed at the 0th, 60th, and 180th cycle points. The onset temperature, peak temperature, and enthalpy were measured at each point to monitor for potential degradation or performance changes. This testing approach facilitates accelerated evaluation of the material's thermal reliability and stability. Prior studies support the use of DSC for such simulations, as seen in the work of Gao *et al*. [40] and Patel *et al*. [41] , where up to 5400 thermal cycles were applied to replicate long-term use over multiple years, with DSC used to track phase change temperatures and latent heat variations. This method allowed for a controlled and accelerated assessment of the PCM's durability and thermal reliability under simulated long-term use and validate the method of simulating prolonged operational conditions for PCMs in building applications. The DSC thermographs for Mixtures E and F throughout these cycles are depicted in Figures 7 and 8, respectively.

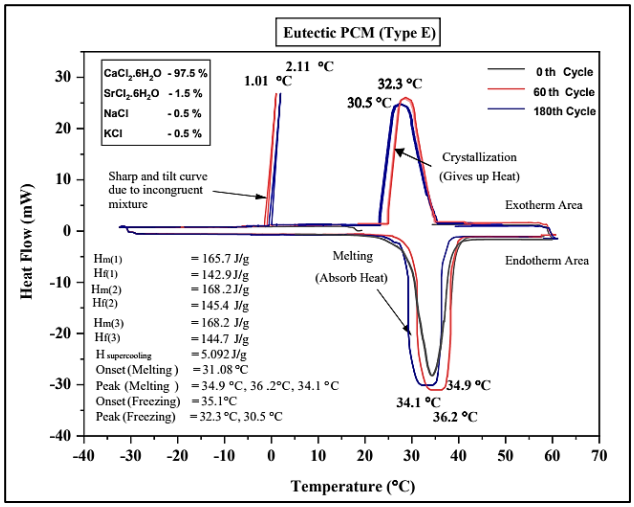

Figure 7 DSC curve at 0th cycle, 60th cycle, and 180th cycle for Mixture E

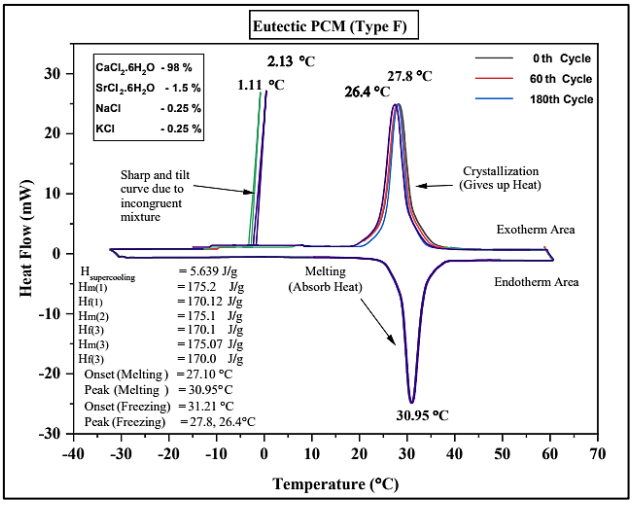

Figure 8 DSC curve at 0th cycle, 60th cycle, and 180th cycle for Mixture F

After 180 thermal cycles, Mixture E displays peak melting and freezing temperatures of 34.10 °C and 30.50 °C, correspondingly, along with enthalpy values of 167.4 J/g and 144.3 J/g. The temperature gaps between melting and freezing after 180 cycles are 2.1°C and 1.8°C, respectively. Conversely, following 180 thermal cycles, Mixture F reveals peak melting and freezing temperatures of 30.95 °C and 26.40 °C, with enthalpy values of 175.2 J/g and 170.1 J/g, respectively.

There is no difference observed in melting temperature at the 180th heat cycle, with a value of 0 %. However, the difference in the freezing point temperature at the 180th cycle is 1.4 °C, representing only a 5.03 % reduction in the value of the freezing temperature at the 180th cycle (26.40 J/g) from the initial value at the 0th thermal cycle (27.80 J/g). The condition of the eutectic mixture at a given temperature during the heating and cooling process is shown in Figure 9.

(a) (b) (c)

Figure 9 Thermal cycle test results. (a) Molten PCM corresponds to the melting process, (b) Crystallisation seed formed during the heating-cooling process, and (c) PCM Crystallized.

The analysis concludes that Mixtures E and F exhibit good thermal stability. Mixture F is identified as a PCM mixture with the potential to become a stable eutectic PCM with the best effect in reducing the indoor temperature of the building. This is due to its melting phase change temperatures fluctuating within the narrow range of 30.95 °C, possessing an enthalpy of 175.2 J/g after undergoing 180 thermal cycles. Table 7 presents a summarized comparison of the DSC curve of these mixtures pre and post 180 heating-cooling cycles.

Table 7 presents a summarized comparison of the DSC curve of these mixtures pre and post 180 heating-cooling cycles. The stability of this melting point (~30.95 °C) corresponds closely to the average daily ambient temperature range observed in Malaysia's tropical climates (28-32 °C) [42][43][44], further confirming its suitability for thermal energy storage in such regions.

Table 7 Summary of supercooling degree

Mix.	T_m – Peak (°C)		T_f – Peak (°C)		μ H_m (J/g)	μ H_f (J/g)	Δ T_m (°C)	ΔT_f (°C)
	0th cycle (a)	180th cycle (b)	0th cycle (c)	180th cycle (d)			(a) – (b)	(c) - (d)
E	36.20	34.10	32.30	30.50	167.4	144.3	2.1	1.8
F	30.95	30.95	27.80	26.40	175.2	170.1	0	1.4

***Notes:**
μ H_m= Average melting enthalpy
μ H_f= Average freezing enthalpy
Δ T_m= Peak melting temperature difference at 180th
Δ T_m= Peak freezing temperature difference at 180th
Δs= Supercooling degree after 180th thermal cycles

4.0 CONCLUSION

This study has successfully demonstrated the improvement of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) as a phase change material (PCM) by incorporating strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$), sodium chloride (NaCl), and potassium chloride (KCl). The combination of these additives proved effective in reducing supercooling and improving the phase stability of the PCM composites. Among the compositions tested, Mixture F, comprising 1.5 wt.% $SrCl_2 \cdot 6H_2O$, 0.25 wt.% NaCl, and 0.25 wt.% KCl stood out for reducing the supercooling degree to 3.15°C, leading to an 84.6% decrease compared to pure $CaCl_2 \cdot 6H_2O$, which exhibited a supercooling degree of 20.45°C.

Thermal stability tests over 180 thermal cycles confirmed the reliability of the modified $CaCl_2 \cdot 6H_2O$. Mixture F showed consistent melting and freezing temperatures at 30.95°C and 26.40°C, respectively, with a minimal 5.03% decrease in freezing temperature and a maximum deviation of only 0.1% in latent heat. Similarly, Mixture E demonstrated robust phase stability, maintaining melting and freezing temperatures at 34.10°C and 30.50°C after 180 cycles, with a supercooling degree of 3.6°C.

Although the increase in latent heat capacity (4.65%) appears modest, its significance les n being achieved alongside an 84.6% reduction in supercooling and strong thermal stability across 180 heating-cooling cycles. In the context of PCM research, such trade-offs are important, as decreases in stability or higher supercooling.

These results highlight the potential of Mixtures E and F for TES applications, particularly in climates with high ambient temperatures, such as those in Malaysia. Enhanced thermophysical properties and phase stability position these materials as strong contenders for eco-friendly thermal energy storage solutions in building applications.

5.0 RECOMMENDATION ON FUTURE WORK

For future research, it is recommended to investigate the integration of the optimized eutectic PCM mixtures into building materials and structural components to enable large-scale thermal energy storage systems for both residential and commercial use. Such advancements could significantly reduce energy consumption, particularly in cooling systems, and promote sustainability in building design.

Additionally, further studies should focus on developing effective encapsulation techniques for these eutectic PCMs to enhance their thermal performance and durability. Encapsulation would allow for the more efficient incorporation of PCMs into building components, improving heat transfer while maintaining the structural integrity of the materials.

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Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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