



Article

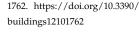
Optimization of Preparation Method, Nucleating Agent, and Stabilizers for Synthesizing Calcium Chloride Hexahydrate (CaCl₂.6H₂O) Phase Change Material

Jay Thakkar ¹, Nicholas Bowen ¹, Allen C. Chang ¹, Peter Horwath ², Margaret J. Sobkowicz ¹ and Jan Kośny ^{3,*}

- Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, MA 01854, USA
- ² Insol Corp., Albemale, NC 28001, USA
- ³ Department of Mechanical Engineering, University of Massachusetts Lowell, Lowell, MA 01854, USA
- * Correspondence: jan_kosny@uml.edu

Abstract: This study investigates improvements in low-cost latent heat storage material calcium chloride hexahydrate (CaCl₂.6H₂O). Its melting point is between 25 and 28 °C, with relatively high enthalpy (170–190 J/g); however, this phase change material (PCM) shows supercooling and phase separation. In CaCl₂.6H₂O incongruent melting causes lower hydrates of CaCl₂ to form, which affects the overall energy storage capacity and long-term durability. In this work, PCM performance enhancement was achieved by adding SrCl₂.6H₂O as a nucleating agent and NaCl/KCl as a stabilizer to prevent supercooling and phase separation, respectively. We investigated the PCM preparation method and optimized the proportions of SrCl₂.6H₂O and NaCl/KCl. Thermal testing for 25 cycles combined with DSC and T-history testing was performed to observe changes in enthalpy, phase transitions and supercooling over the extended period of usage. X-ray diffraction was used to verify crystalline structure in the compounds. It was found that the addition of 2 wt.% of SrCl₂.6H₂O reduced supercooling from 12 °C to 0 °C compared to unmodified CaCl₂.6H₂O. The addition of 5 wt.% NaCl or KCl proved to effectively suppress separation and the melting enthalpy achieved was 169 J/g–178 J/g with congruent melting over 25 cycles, with no supercooling and almost no reduction in the latent heat.

Keywords: latent heat storage; PCM; building application; CaCl₂.6H₂O; supercooling; phase separation; thermal cycles



check for

updates

Citation: Thakkar, J.; Bowen, N.;

M.J.; Kośny, J. Optimization of

Agent, and Stabilizers for Synthesizing Calcium Chloride

Preparation Method, Nucleating

Hexahydrate (CaCl₂.6H₂O) Phase Change Material. *Buildings* **2022**, 12,

Chang, A.C.; Horwath, P.; Sobkowicz,

Academic Editor: Francesco Asdrubali

Received: 26 July 2022 Accepted: 7 October 2022 Published: 21 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Energy demands have exponentially increased over the past few decades, leading to massive consumption of fossil fuels all over the world. The depletion of fossil fuels resources has accelerated work towards sustainable energy sources, but the detrimental effects of fossil fuel use remain a threat to the environment. The building sector is a frontrunner in energy consumption. Building energy demand is projected to rise by about 50% by 2050 worldwide [1]. The majority of this energy consumption is related to heating ventilation and air conditioning (HVAC) systems; demand for this energy could be mitigated via improved thermal performance of building envelope materials [2]. Thermal energy systems (TES) are a solution to improve the energy efficiency of the building sector [3]. TESs store thermal energy and release that same energy at a later time as a passive heating and cooling application [4]. Two parts of TES include latent heat storage (LHS) and sensible heat storage. LHS changes temperature with a change in material phase, while sensible heat changes temperature while leaving the phase of the TES material unaltered. Comparisons between LHS and sensible heat storage suggest that LHS performed better when evaluating capacity, power, storage duration and cost [5].

Phase change materials (PCMs) for LHS, which store and release energy by melting and cooling, are steadily improving. PCMs are available with a wide range of melting

Buildings 2022, 12, 1762 2 of 19

temperatures with high storage density. Their stable performance and low cost make them highly pursued for various applications in thermal management, including cold chain shipping, renewable energy storage, photovoltaics and electronics cooling, and personal thermal management [6]. PCMs typically fall into two distinct categories: organic (e.g., paraffins and non-paraffins) and inorganic [7]. Among these, salt hydrates are the most important and widely researched group of inorganic PCMs because of their low cost, wide availability, good thermal conductivity, high melting enthalpy and desirable melting temperature range [8]. In salt hydrates, nH_2O represents the number of water molecules associated with each salt complex. As the water content decreases, the melting point of the salt hydrate increases [9]. The salt crystal is solid, but it may contain more than 50% of water by mass. When the salt hydrate crystal is heated it melts and the water of crystallization is released, into which the salt ions dissociate. Most salt hydrate PCMs have very low health and safety risks and are naturally abundant. Inorganic PCMs can have melting points anywhere from 5 °C to 130 °C, and many salt hydrates melt congruently without phase separation, retaining the exact chemical composition as the solid phase. Some of the congruently melting salt hydrates are, LiClO₃.3H₂O, NaOH.3.5H₂O, KF.4H₂O, Zn(NO₃)₂.6H₂O, NaOH.H₂O and Mg(NO₃).6H₂O [10]. Encapsulation of PCM in LHS for buildings is a cost-effective and safe approach. In microencapsulation, PCMs are packed in small, spherical or rod-shaped particles, whereas in macroencapsulation, PCMs are enclosed in tubes, pouches, panels or containers [11]. In contrast to many organic PCMs, salt hydrates are compatible with plastic packaging. Selection of a proper container for PCM packaging is important because undesirable reactions between the packaging material and PCM can affect its performance. Plastics are currently used to encapsulate PCM but compatibility testing for long term product stability is required. Studies on compatibility of salt hydrates with polyethylene (HDPE), polypropylene (PP) and polyvinylchloride (PVC) showed negligible mass change of plastics when placed in contact with salts compared to organic PCM [12]. Due to the corrosiveness of salt hydrate based PCMs, the long-time durability of metal packaging is arguable. Stainless steel, carbon steel, aluminum alloys and copper have been tested with salt hydrates of different melt temperatures. Stainless steel was found to be the most corrosion resistant followed by copper, which initially corroded, but remained stable over a longer time. Calcium chloride had no corrosion effect on copper. Aluminum has been found compatible with sodium acetate based PCM [13]. Another major advantage of salt hydrate PCMs over organic PCMs is that these inorganic PCM are inherently non-flammable.

Despite the aforementioned attractive properties, salt hydrates exhibit many problems which must be resolved before they can be commercialized for practical applications. Issues with salt hydrates include change of volume at phase transition, supercooling, phase separation, corrosion and loss of water upon cycling [14]. Supercooling is considered to be a major disadvantage of salt hydrates, resulting from insufficient nucleation. Supercooling is a condition where the solidification of the PCM is delayed to below the melting point, requiring a wider operating temperature range. If solidification does not occur at the desired temperature, the PCM is unable to release the crystallization heat right below the melting point and the long-term stability can be affected. There are two supercooling scenarios: poor nucleation means delay of crystallization because of no nucleation sites for the crystal to grow or there is no effect of any nucleating agent if added and poor crystal growth rate relates to crystallization kinetics. For most of energy related applications, it is necessary to suppress the supercooling as it limits the widespread usage of PCMs [15]. Supercooling can be suppressed by either adding nucleating agents that have similar crystal structures to the PCM, or by seeding with a solid crystal of the same material as PCM. It can also be suppressed by agitation, electrical, mechanical and ultrasound means. There are limitations with all these methods, but the most preferred method is the addition of nucleating agent as it has been shown to suppress supercooling by more than 90% with small proportion (1%) of material [16].

Buildings **2022**, 12, 1762 3 of 19

Another challenge is incongruent or semi-congruent melting/freezing behavior of salt hydrates, which leads to phase separation. Incongruent melting changes the composition of the material, forming two different salt hydrates that melt at different temperatures, whereas semi-congruent melting means that only a portion of anhydrous salt forms the desired salt hydrate, which leads to loss of energy. The amount of water released in dehydration is not enough for the complete dissolution of the salts, which leads to formation of secondary phases of less hydrated PCMs; these secondary phases may erode the intended thermal storage behavior. It is important to be aware of the possible other hydrates in a particular PCM system to formulate final products such that incongruent melting is avoided. There are many methods used to eliminate this phase separation such as the addition of different stabilizers or thickening agents, addition of extra water, and mechanical stirring to reach and maintain the eutectic point of PCM. It is critical to determine a method that works well to stabilize the PCM over many thermal cycles, especially for building applications [17].

Thermal cycling testing, supporting durability analysis, is another important factor that needs to be undertaken in order for building thermal storage systems to be commercialized. The initial thermal cycling just after the preparation of PCM formulations is critical because some PCMs do not yield the expected latent heat until the crystallization process is perfected, and others may not be stable after couple first cycles. Erosion of the melting enthalpy over repeated cycling can be indicative of incongruent melting and large-scale phase separation, dehydration, and inhomogeneous heat distribution throughout the material. That is why it is recommended that accelerated thermal cycle tests should be performed in the lab conditions before the commercialization or production scale up. It is also important to consider the effects of the heating and cooling rates as the PCM performance may vary depending on the thermal cycle time.

There are many inorganic salt hydrate PCMs with melting temperatures between 30–36 °C such as sodium carbonate decahydrate (Na $_2$ CO $_3$.10H $_2$ O), sodium sulfate decahydrate (Na $_2$ SO $_4$.10H $_2$ O) and di-sodium hydrogen phosphate do-decahydrate (Na $_2$ HPO $_4$.12H $_2$ O), etc., which exhibit supercooling and phase separation defects. Phase change behaviour of these PCMs can be improved by adding nucleating agents and stabilizers/thickening agents. There are also eutectic—salt hydrate-based PCMs, such as Na $_2$ CO $_3$.10H $_2$ O—Na $_2$ SO $_4$.10H $_2$ O, Na $_2$ HPO $_4$.12H $_2$ O—Na $_2$ SO $_4$.10H $_2$ O and many more, all of which have phase transition temperatures around 30–35 °C. Once again, defects in these materials exist and need to be addressed by adding nucleating and thickening agents [18,19]. However, for building applications, CaCl $_2$.6H $_2$ O with melt temperature between 25 and 30 is most suitable.

Calcium chloride hexahydrate (CaCl $_2$.6H $_2$ O) is an example of inorganic salt hydrate which has garnered much attention in the past and still has potential for additional investigation and improvement. It exhibits phase transition in temperature range between 25 and 30 °C, with reported high latent heat between 170 and over 200 J/g. Thermal conductivity of this PCM for solid and liquid is 1.08 and 0.56 Wm $^{-1}$ K $^{-1}$, respectively, and solid and liquid density of CaCl $_2$.6H $_2$ O is 1710 Kgm $^{-3}$ and 1560 Kgm $^{-3}$ making it an ideal PCM for building applications [20]. CaCl $_2$.6H $_2$ O based PCM has a working temperature range in human comfort; thus, its use in building applications has been studied by packaging in panels used as wall/ceiling or floor tiles (see: Figure 1). This results in an improvement of indoor thermal comfort and enhances heat storage capability [21]. Despite this, CaCl $_2$.6H $_2$ O faces a major challenge, in that supercooling and semi-congruent melting lead to undesirable phase separation [22].

PCM formulations using CaCl₂.6H₂O have a long history of research and usage for building applications. In 1984, a high melting enthalpy of 209 J/g was reported for CaCl₂.6H₂O with a melting point of 29 $^{\circ}$ C. In this work, crystal nucleation was required to prevent supercooling [23]. SrCl₂.6H₂O is used as a nucleating because of its similarity in crystal structure to CaCl₂.6H₂O. SrCl₂.6H₂O has also been shown to help solubilize the CaCl₂.6H₂O. Incongruent melting of CaCl₂.6H₂O can be controlled through addition of calcium hydroxide. An increase/decrease in the melting point was achieved with the

Buildings 2022, 12, 1762 4 of 19

several additives such as $MgCl_2.6H_2O$, KNO_3 , etc., however they are eutectic PCM [24]. Researchers have also tested the effects adding 1–5 wt.% of KCl, NaCl and LiCl on melting temperature and crystallization temperature. They also suggested barium salts as nucleating agent for this PCM as the dimensions are similar to the $CaCl_2.6H_2O$ [25]. On addition of KCl alone, supercooling was not suppressed. It was observed that at least 5% of KCl should be added to prevent phase separation [26]. The effect of excess water in preventing dehydration has been studied for over 1000 cycles. They changed the stoichiometric composition of this PCM but kept the composition less than the peritectic point which resulted in suppression of tetrahydrates. NaCl was utilized here to repeat the phase change repeatability but was not used as a nucleating agent [27]. In terms of durability, thermal testing of $CaCl_2.6H_2O$ without any additives was carried out for 1000 cycles. Stability of latent heat (120–125 J/g) and melting point (23–25 °C) was observed during this testing with no phase separation [28].

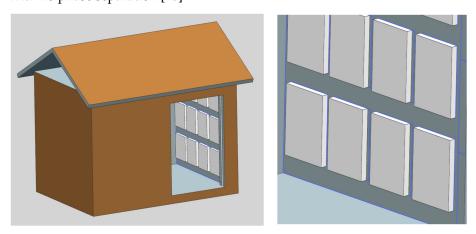


Figure 1. Example of the PCM usage in a small house/hut/container where PCM panels are installed on walls.

The relationship between CaCl₂.2H₂O and anhydrous CaCl₂ has been investigated. This work concluded that increasing proportion of CaCl₂.2H₂O decreased the supercooling in this PCM. It was found that supercooling reduced to 0.8 °C when the proportion of CaCl₂.2H₂O was 66.21%. They also used silicon dioxide (SiO₂) as a nucleating agent which eliminated the supercooling [29]. XRD analysis of prepared CaCl₂.6H₂O was done to verify the purity of the sample by comparing it with standard crystallography data. Graphene oxide has also been used to suppress supercooling; on addition of 0.02% graphene oxide supercooling reduced by 61.6% whereas addition of 0.8% SrCl₂.6H₂O (nucleating agent) reduced supercooling by 76.5%. When both the materials were added together, it suppressed supercooling by 99%. It concluded that supercooling cannot be eliminated completely with independent use of nucleating agent [30]. Table 1 summarizes reported results for CaCl₂.6H₂O with various nucleating agents and stabilizers.

All these cited above studies illustrate the wide array of nucleation agents and stabilizers, compositions and the complex phase behavior observed in the CaCl₂.6H₂O system. However, systematic analysis of the influence of multiple additives has not been reported yet for this family of PCMs. The formulation material composition as well as the preparation method for this salt hydrate are critical for the PCM performance, and so far, very few publications explain in detail all formulation preparation steps. The present work reports on two preparation methods for CaCl₂.6H₂O resulting in a single phase PCM. Suppression of supercooling is explored using different amounts of SrCl₂.6H₂O. The effect of different proportions of SrCl₂.6H₂O on supercooling and latent heat was also discussed. The expected result on addition of SrCl₂.6H₂O is to have no supercooling for multiple cycles. NaCl and KCl are explored as stabilizers of the hexahydrate form of CaCl₂ for phase stability. The influence of each additive and their combinations is systematically studied using DSC, XRD and T-history methods over multiple cycles. In this work, stability testing

Buildings 2022, 12, 1762 5 of 19

was done up to 15 cycles and stable combinations were carried out to 25 cycles to check for continuous PCM behavior.

Table 1.	Inorganic	salt hyd	lrates	PCM.

Sr No.	Nucleating Agent	Stabilizer	Supercooling	Cycles	Latent Heat	Reference	
1	GO + SrCl ₂ .6H ₂ O (0.02 % + 0.8 %)	-	1.7	250	198	[30]	
2	SrCl ₂ .6H ₂ O (3%)	KCl (2%)	≤2	100	170	[31]	
3	EG	-	NA	NA	118	[21]	
	SrCl ₂ .6H ₂ O (3%)	-	2	1			
	Graphite (3%)	-	15.5	1		_	
4	FeO (3%)	-	3.8	1		[31]	
	Ca(OH) ₂ (3%)	-	16	1		_	
	Wood	-	6.2	1			
5	-	-	-	1000	125	[28]	
	BaCO ₃ (0.5%) BaCO ₃ (0.5%)	-	0.59 0.58	15 10	-	[00]	
6	K ₂ CO ₃ (0.5%) K ₂ CO ₃ (1%)	-	1.07 0.73	13 10	-	- [32]	
_	SrCl ₂ .6H ₂ O	-	1		-	[22]	
7	Ba(OH) ₂ .8H ₂ O	-	No effect		-	- [33]	
	BaI ₂ (0.5%)	-	0	20	-		
8	BaSO ₄ (0.1%)	-	0–5 0–1.5	170 281	-	[34]	
	BaO	-	0–3	25	-	_	
	SrCl ₂ .6H ₂ O (2%)	KCl (5%)	0	25	169	T .1.	
9	SrCl ₂ .6H ₂ O (2%)	NaCl (5%)	0	25	178	In this research	

This publication discusses only the development and optimization of the $CaCl_2.6H_2O$ based PCM formulations, as well as early thermal performance test results from the multi-year project which also includes the field performance testing and thermal cycling for up to 2000 cycles, which will be discussed in the following reports.

2. Materials and Methods

2.1. Materials

All the materials were obtained from Carolina Biological Supply Company, Burlington, North Carolina, and used as received. Calcium Chloride dihydrate (CaCl₂.2H₂O, granular laboratory grade) which contained calcium chloride anhydrous (77–80%), water (15–20%), Potassium chloride (2–3%) and Sodium chloride (1–2%) was used to prepare Calcium chloride hexahydrate (CaCl₂.6H₂O). Sodium chloride (NaCl, ACS grade) and Potassium chloride (KCl, granular, ACS grade) were used as stabilizers. Strontium chloride hexahydrate (SrCl₂.6H₂O, 100% pure, ACS grade) was used as a nucleating agent. Distilled water was used for this research work.

Preparation Method

In this paper, two methods were used to prepare 20 g batches of $CaCl_2.6H_2O$. In the first method, $CaCl_2.2H_2O$ and water were weighed using an analytical balance (Mettler Toledo) to achieve the stoichiometry of $CaCl_2.6H_2O$ ($CaCl_2.6H_2O$ = 111:108). The molar mass of $CaCl_2.2H_2O$ is 147 g/mol; in order to prepare $CaCl_2.6H_2O$, 13.42 g of $CaCl_2.2H_2O$ and 6.58 g of distilled water were mixed together in glass vials. The mixture was placed on the hot plate (VWR Scientific) and temperature was maintained at 60 °C until it completely melted. After complete melting was achieved, it was stirred on a magnetic stir plate for

Buildings 2022, 12, 1762 6 of 19

about 30 min to get a uniform mixture of $CaCl_2.6H_2O$. The PCMs were then allowed to cool down at room temperature and placed in the refrigerator overnight. In the second method, no heating was applied to prepare $CaCl_2.6H_2O$ in order to minimize evaporation of water. On adding $CaCl_2.2H_2O$ in water, the temperature rises to 40 °C because of the exothermic enthalpy of mixing. $CaCl_2.2H_2O$ and water were mixed in the same proportion as method one and stirred with a magnetic stir bar continuously until complete melting was achieved. The temperature of the mixture was not allowed to exceed 40 °C. After complete melting it was allowed to cool down at room temperature and placed in the refrigerator overnight. Figure 2 shows the preparation method used in this research work.

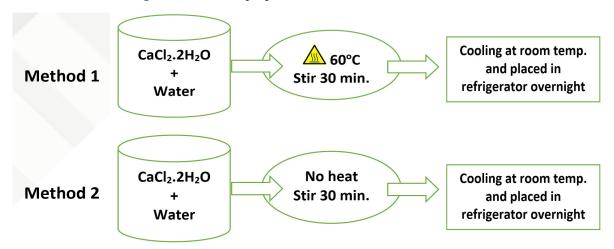


Figure 2. Preparation method used for synthesis of CaCl₂.6H₂O.

2.2. Modification of CaCl₂.6H₂O with Additives

In order to achieve a stable PCM, both stabilizer and nucleating agent were added following the Design of Experiments in Table 2. SrCl₂.6H₂O was used to prevent the supercooling in CaCl₂.6H₂O, whereas KCl and NaCl were added to stabilize the PCM in its hexahydrate form supporting congruent melting. Three weight percentages (2, 3 and 5%) of each additive were mixed into the melted CaCl₂.6H₂O. Samples were continuously stirred with the help of stir bars and the temperature of the hot plate was maintained at 40 °C until complete melting was achieved, as confirmed by visual observation.

CaCl ₂ .6H ₂ O		SrCl ₂ .6H ₂ O			KCl			NaCl	
	2%	3%	5%	2%	3%	5%	2%	3%	5%
100%									
98%	X								
97%		X							
95%			X						
98%				Χ					
97%					X				
95%						X			
98%							Χ		
97%								X	
95%									X
			Combination	on of two addi	tives withCaC	l ₂ .6H ₂ O			
96%	Х						Х		
95%	X							X	
93%	X								X
96%	X			X					
95%	X				X				

Χ

93%

Table 2. CaCl₂.6H₂O design of experiment with different proportion of nucleating agent and stabilizer.

Χ

Buildings **2022**, 12, 1762 7 of 19

3. Characterization Methods

Differential Scanning Calorimetry (DSC): In this research, DSC testing was performed to find the melting onset temperature, peak temperature and latent heat of the PCM. The DSC equipment used for this testing was Discover Q20, TA instruments (Newcastle, DE, USA). Analysis of the results was carried out in the TA Universal Analysis software. Amounts of 5–10 mg of samples were placed in aniodic coated aluminum pans. The heating rate was kept at 2 $^{\circ}$ C/min. with temperature range of -15 $^{\circ}$ C to 60 $^{\circ}$ C. For multiple cycle measurements, samples were heated and cooled at a rate of 2 $^{\circ}$ C/min outside of the instrument, and then a DSC sample was prepared from the cycled bulk sample.

Temperature history method (T-history): This method was developed for getting the thermal properties of the PCM for larger sample size. T-history method has been used to analyze/estimate PCM melting point, latent heat of fusion, supercooling, specific heat, and thermal conductivity for bulk materials. Thermal properties obtained from this testing can be compared to the data obtained from DSC to understand the effects of sample volume. In this research we utilized the T history method to record the supercooling degree [34]. Heating and cooling of the PCM samples were done in a water bath in which the water temperature was not held constant. Thermocouples (T type resolution) were used to measure the temperature. The thermocouple was placed in the sample and was connected to a data logger (CR 3000, Campbell Scientific, Logan, UT, USA) which recorded the temperature. Figure 3 shows the T-history test setup showing the water bath, datalogger and the laptop connected to use the PC200 software (version 4.5).

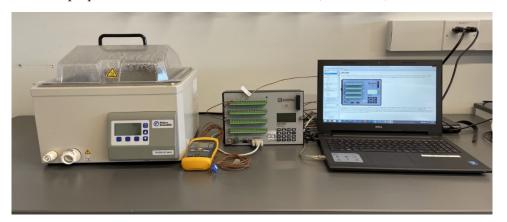


Figure 3. T-history setup for measuring supercooling.

X-ray diffraction (XRD): XRD analysis was done to verify the presence of the hexahydrate of calcium chloride depending on preparation method, and also to compare the data of the salt hydrate without any additives and with additives. The crystal analysis of CaCl₂.6H₂O was carried out by X-ray powder diffractometer (AXRD Proto Benchtop, Proto Manufacturing, Taylor, MI, USA) with CuK α radiation, which has a characteristic wavelength of 1.5418 Å. The diffraction patterns were collected over a 20 range of 10° to 50° . The samples were ground loaded into the XRD sample holder. The diffraction patterns obtained from the software XRD WINPD were smoothed in the Origin software. The peak identification was also done in Origin software. The diffraction patterns for two different preparation methods of CaCl₂.6H₂O were compared with the standard XRD data.

4. Results and Discussion

4.1. Analysis Supporting CaCl₂.6H₂O Preparation

The DSC testing was performed to compare the phase change behavior for both the samples. It can be seen in Figure 4, the sample prepared without the heating had a single peak for PCM melting. This means there is no phase separation (e.g., formation of $CaCl_2.4H_2O$). For the other sample, which was prepared with heating, two melting peaks can be observed which means $CaCl_2.4H_2O$ co-exists with the $CaCl_2.6H_2O$. Additionally, the

Buildings **2022**, 12, 1762 8 of 19

phase change enthalpy is significantly lower for the PCM prepared with heating—145 J/g compared to the sample prepared with heating at 172 J/g. Based on these results, it can be concluded that synthesis of CaCl₂.6H₂O, should not include the heating process.

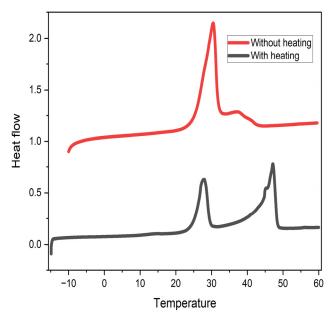


Figure 4. DSC curve of CaCl₂.6H₂O showing the first melt cycle for both the preparation method.

XRD analyses of $CaCl_2.6H_2O$ for both the samples was performed to verify the structure of the crystals present in the PCM. Figure 5 shows the XRD data for both the samples. Diffraction patterns of both the prepared samples of $CaCl_2.6H_2O$ were compared with the reference results of $CaCl_2.6H_2O$ which was obtained from the Standard X-ray Diffraction powder patterns published by Institute of Material Research under National Bureau of Standards [35]. Table 3 shows the comparison for the samples with the peak location (diffraction patterns) in 20. $CaCl_2.6H_2O$ without heating has almost the same location for the peaks as the reference sample peaks whereas for sample prepared with heating, peaks are missing. From these data, it is clear that the sample prepared without heating has similar diffraction patterns to the reference for $CaCl_2.6H_2O$, which means it actually contains the hexahydrate part of the PCM. While no reference is available for the tetrahydrate form, the sample prepared with heating shows a weaker diffraction pattern missing many of the peaks identified as hexahydrate.

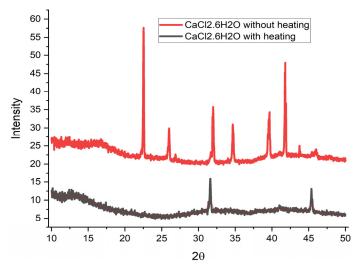


Figure 5. XRD pattern of CaCl₂.6H₂O showing peak location and intensity of crystals.

Buildings **2022**, 12, 1762 9 of 19

CaCl ₂ .6H ₂ O Sample Prepared without Heating (2θ) °	CaCl ₂ .6H ₂ O Sample Prepared with Heating (2θ) °	CaCl ₂ .6H ₂ O Reference Sample (2θ) °
-	12.5	13
22.6	-	22.6
26.0	-	26.0
32.0	31.5	32.0
34.9	-	34.7
39.6	-	39.6
41.8	41.0	41.8
45.0	45.4	45.8
47.0	-	47.8

Table 3. Peak location of the XRD plot.

4.2. Analysis of Supercooling Effect in CaCl₂.6H₂O

The T-history method was used for analyzing the magnitude of supercooling in $CaCl_2.6H_2O$. It was observed that upon increasing the number of heating-cooling cycles, the supercooling level also increased. Cooling curves can be seen in the Figure 6a for $CaCl_2.6H_2O$. The temperature spike observed during cooling is indicative of the phase transition occurring below the thermodynamic freezing temperature (~25 °C). The amount of supercooling is taken to be the height of the spike (e.g., 12 °C for the 15th cycle in Figure 6b). The bar graph shows the increase in the supercooling of this PCM with the increase in heating-cooling cycle. The increase in supercooling must be controlled as it leads to the decrease in available phase change energy; $SrCl_2.6H_2O$ was added in different proportions as a nucleating agent to suppress the supercooling.

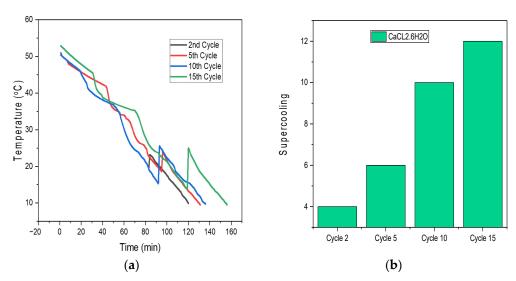


Figure 6. (a) T-history curve for 15 cycles for CaCl₂.6H₂O; (b) Increase in Supercooling graph for CaCl₂.6H₂O.

4.3. Analysis of Phase Separation in CaCl₂.6H₂O

DSC testing was used to find the melting temperature and latent heat of melting. The DSC curves shown in Figure 7a is for pure $CaCl_2.6H_2O$. The melting point was found to be 25.2 °C with latent heat of 172 J/g. As the number of heating-cooling cycles increases, it can be seen in Figure 7a, melting range increases for $CaCl_2.6H_2O$ which means it starts losing water to form lower hydrates leading to incongruent melting. For cycle 15, the peak temperature is 47.1 °C which proves the presence of $CaCl_2.4H_2O$ in the sample (see Figure 7a). A supernatant liquid was observed during the thermal cycles. Figure 7b shows

Buildings **2022**, 12, 1762 10 of 19

anhydrous salt settled at the bottom indicating separation of $CaCl_2.6H_2O$ into $CaCl_2.4H_2O$ at the time of freezing. Also, the latent heat of melting decreases with the increasing thermal cycles. Table 4 shows the melting temperature, peak temperature and latent heat up to 15 cycles. These results show that $CaCl_2.6H_2O$ is not stable and it is necessary to add stabilizer to prevent the incongruent melting leading to phase separation.

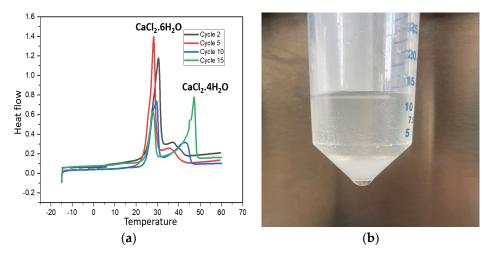


Figure 7. (a) DSC curve for CaCl₂.6H₂O during the first 15 cycles; (b) CaCl₂.6H₂O sample showing phase separation.

Table 4. Melt temperature (T_m), peak temperature (T_p) and enthalpy for CaCl₂.6H₂O up to 15 cycles.

Cycle No.	T _m (°C)	T _p (°C)	Enthalpy (J/g)
2	25.2	30.4	172
5	24.8	29.5	152
10	24.9	29.4	148
15	25.1	47.1	145

4.4. Analysis of Modified CaCl₂.6H₂O with Stabilizer and Nucleating Agent

4.4.1. Addition of Nucleating Agent

SrCl₂.6H₂O was added in 2, 3 and 5 wt.% to the CaCl₂.6H₂O. It is theorized that this salt hydrate has a similar crystal structure to CaCl₂.6H₂O which allows the crystal growth (nucleation). The epitaxy effect is exploited as the CaCl₂.6H₂O is exposed to a surface of similar crystal unit cell where nucleation takes place, facilitating growth of the crystals of CaCl₂.6H₂O. Epitaxy effect is providing a surface by the nucleating agent to have crystal growth, which in this CaCl₂.6H₂O PCM is exhibited by SrCl₂.6H₂O. Figure 8 shows the suppression of supercooling for different proportions of added SrCl₂.6H₂O during T-history testing. Initially supercooling was notably decreased to 1 °C for all the different proportions of SrCl₂.6H₂O up to 5 cycles, however on increasing the thermal cycles it can be seen that supercooling increased for 3 and 5 wt.% to 3 °C and 4 °C for 10th cycle and 5 °C and 6 °C for 15th cycle, respectively. As the proportion of SrCl₂.6H₂O increases, a SrCl₂ rich phase is present that is no longer effective as a nucleating agent. This finding leads to the conclusion that minimal quantity of SrCl₂.6H₂O is required for effective and repeatable nucleation effect on the PCM. DSC testing was also done for these samples to check the impact on the latent heat of the PCM. Latent heat was found to be 182 J/g for 2 wt.% whereas on increasing SrCl₂.6H₂O to 3 wt.% and 5 wt.% resulted in decrease of about 20% and 23% of latent heat to 150 J/g and 144 respectively. Figure 9 shows the trend of decreasing latent heat with the increasing proportion of SrCl₂.6H₂O.

For further investigations, we considered 2 wt.% of SrCl₂.6H₂O as the optimum proportion to prevent supercooling.

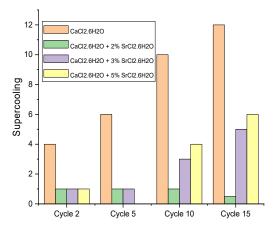


Figure 8. Supercooling degree comparison with SrCl₂.6H₂O for different heating cycle.

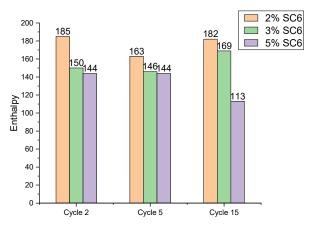


Figure 9. Enthalpy comparison for different proportion of SrCl₂.6H₂O for increasing thermal cycles.

4.4.2. Addition of Stabilizers to Prevent Incongruent Melting

KCl and NaCl were added separately with CaCl₂.6H₂O in three different proportions (2, 3 and 5 wt.%) to produce a stable PCM with congruent melting and to prevent the formation of lower hydrates of CaCl₂. On the addition of KCl, the melting range of the PCM was broad, which means that a part of hexahydrate released water to form CaCl₂.4H₂O. It can be clearly seen in Figure 10a for DSC curve of 2 wt.% KCl, there are two melting peaks leading to phase separation after up to 5 cycles. After 10 cycles, PCM stabilized with congruently melting. This was not maintained long—only till 15 cycles. This experiment shows that the addition of 2 wt.% KCl was not enough to stabilize the hexahydrate. Table 5 shows the melting point, peak temperature and the melting enthalpy for the PCM. The enthalpy also reduced for 2 wt.% of KCl by about 25% when compared to CaCl₂.6H₂O (172 J/g) without any stabilizer. The trend was similar (Figure 10b) for 3 wt.% KCl, the melting range was extended to higher temperature but after 15 cycles enthalpy was observed to be higher by 5% (180 J/g) compared to CaCl₂.6H₂O without KCl. For 5 wt.% of KCl, it can be seen in Figure 11a that the formation of CaCl₂.4H₂O decreases with the increase in thermal cycle. Peak temperature also decreased, and the peak was narrower with the increasing thermal cycles, indicating the formation of a eutectic point where the entire PCM melts at the equilibrium temperature of the system. The enthalpy for 5 wt.% KCl after 15 cycles is almost same as CaCl₂.6H₂O without KCl. Supercooling was observed for all weight percents of KCl which can be seen in Figure 11b. For 5 wt.% KCl, supercooling was decreasing with the increase in thermal cycles.

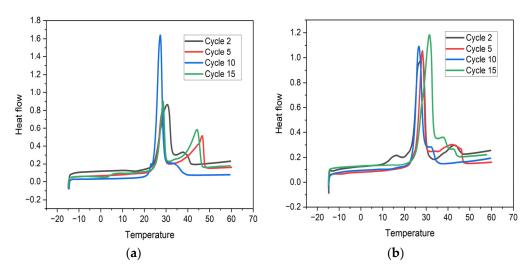


Figure 10. DSC curves showing multiple cycles (a) CaCl₂.6H₂O + 2wt.% KCl; (b) CaCl₂.6H₂O + 3wt.% KCl.

Table 5. Reported data of	CaCla 6HaO with KCl	(2. 3 and 5 wt %) from	n DSC and T-history
Table 3. Nebbited data of	CaCi).0ii)O willi KCi	. Z. 3 and 3 wt. /01 mon	

Composition	Cycle No.	T _m (°C)	Peak Temp. (°C)	Enthalpy (J/g)	Supercooling (°C)
	2	24.6	30.6	146	8
CaCl (H O + 20/ VCl	5	25.5	28	144	6
$CaCl_2.6H_2O + 2\% KCl$	10	25.8	28.6	158	11
_	15	25.5	28	148	12
	2	23.7	28.7	148	8
CaCl ₂ .6H ₂ O + 3% KCl -	5	25.3	28.2	157	10
CaCl ₂ .0H ₂ O + 3% KCl -	10	25.4	29	160	10
-	15	26.2	31.4	180	10
	2	25.4	30.4	141	8
CaCl ₂ .6H ₂ O + 5% KCl -	5	25.5	28.9	141	4
CaCl ₂ .on ₂ O + 5% KCl -	10	25.4	28.4	155	3
	15	25.2	27.7	171	3

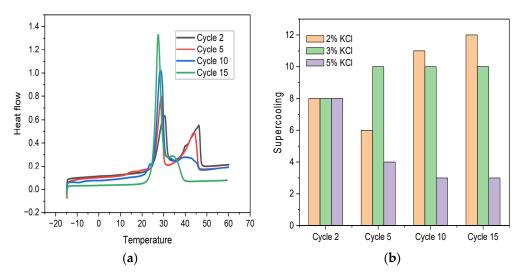


Figure 11. (a) DSC curves of multiple cycles of CaCl₂.6H₂O + 5 wt.% KCl; (b) Supercooling with KCl.

Initially, after the addition of NaCl, the melting point was reduced for all tested formulations. Later, with increasing number of thermal cycles, the melting point increased

and was similar to CaCl₂.6H₂O without additives. For all tested PCM compositions using NaCl, it can be clearly seen in Figure 12a,b, that CaCl₂.4H₂O was formed up to 5 cycles. The results for 10 cycles with NaCl showed a broad melting range implying that some part of the system required higher temperature to melt. For 2 and 3 wt.% of NaCl after 10 cycles, enthalpy was found to be similar to CaCl₂.6H₂O without additives, whereas it was about 5% higher for 5 wt.% of NaCl. After 2 cycles, and again after 15 cycles, the second peak reemerged for 2 wt.% NaCl indicating that it is improper coumpound to stabilize the hexahydrate for congruent melting. For 3 wt.% and 5 wt.% of NaCl, after 15 cycles a small second melting peak was seen, again, indicating the formation of tetrahydrates. Supercooling was also observed with each used proportion of NaCl. Figure 13b shows the supercooling degree for all proportions of used NaCl, indicating the need for a nucleating agent to prevent it. Table 6 shows the data for latent heat, melting point and supercooling with NaCl.

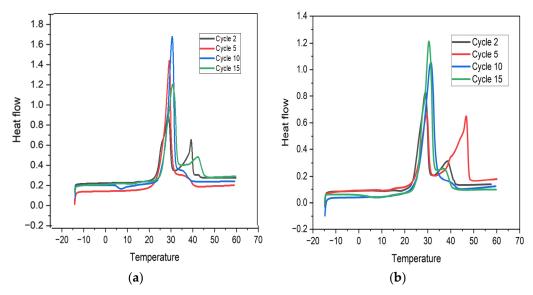


Figure 12. DSC curves of multiple cycles for (a) CaCl₂.6H₂O + 2 wt.% NaCl; (b) CaCl₂.6H₂O + 3 wt.% NaCl.

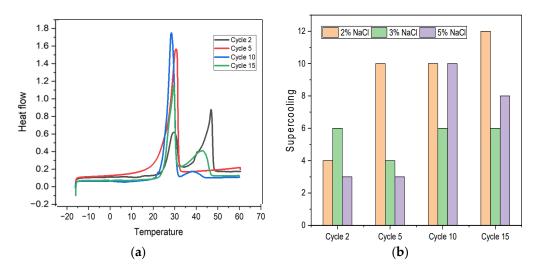


Figure 13. (a) DSC curves of $CaCl_2.6H_2O + 5$ wt.% NaCl; (b) Supercooling for multiple cycles with different proportions of NaCl.

Buildings **2022**, 12, 1762 14 of 19

Table 6. Reported data of CaCl ₂ .6H ₂ O with NaCl (2, 3 and 5 wt.%) from DSC	and T-history.
--	----------------

Composition	Cycle No.	T _m (°C)	Peak Temp. (°C)	Enthalpy (J/g)	Supercooling (°C)
	2	23.1	28.6	129	4
CaCl ₂ .6H ₂ O + 2% NaCl -	5	25.5	28	158	10
CaC12.0H2O + 2/0 NaC1 -	10	25.8	30.2	169	10
_	15	25.5	31.1	158	12
	2	23.9	28.9	132	6
CoCl (H.O., 29/ NoCl	5	24.7	29.5	165	4
$CaCl_2.6H_2O + 3\% NaCl -$	10	26.0	30.4	170	6
_	15	26.5	31.3	185	6
	2	23.4	29.4	135	3
C-Cl (II O : E)/ N-Cl	5	25.15	30.3	142	3
$CaCl_2.6H_2O + 5\% NaCl -$	10	25.4	28.0	196	10
	15	25.2	30.0	180	8

The conclusion from these experiments was that neither NaCl nor KCl alone can effectively stabilize the $CaCl_2.6H_2O$ and prevent supercooling. We hypothesized that combinations of KCl and $SrCl_2.6H_2O$, or NaCl and $SrCl_2.6H_2O$ may help in preventing both effects. That is why the next set of PCM samples was prepared with using $SrCl_2.6H_2O$ and either NaCl or KCl separately.

4.4.3. Analysis of CaCl₂.6H₂O with KCl and SrCl₂.6H₂O

Several mixtures containing 2 wt.% SrCl₂.6H₂O and varying proportions of KCl were tested in DSC and using T-history method for 15 cycles to check the stability of this PCM. For the samples with KCl, initially the melting point decreases for the PCM, but with increasing number of thermal cycles it returns to the same melting point of CaCl₂.6H₂O. Tetrahydrate formation was observed for 2nd cycle and 5th cycle with the melting range extending up to 40 °C. Conducting further heat cycles showed a stable PCM with single melting peak for 3 and 5 wt.% of KCl; however, 2 wt.% KCl continued to show tetrahydrate formation. This means 2 wt.% KCl was not enough to stabilize the CaCl₂.6H₂O. Formation of supernatant liquid was observed after each thermal cycle for 2 wt.% KCl, but not for 3 and 5 wt.% KCl. After 10 cycles, for 3 and 5 wt.% KCl, it can be clearly seen in Figure 14a,b, that there was no tetrahydrate formation. The stable behavior was seen through 15 cycles for both 3% and 5%. However, two melting peaks reappeared in the 3 wt.% KCl after 20 and 25 cycles. The 5 wt.% KCl sample was stable up to 25 cycles with a single melting peak and no tetrahydrate formation was found. Based on the above finings, we believe that 5 wt.% KCl is the eutectic composition for this PCM, yielding a single stable phase and suppressed formation of tetrahydrates. Tables 7 and 8 show the melting temperature, peak temperature, latent heat and supercooling for 3 and 5 wt.% of KCl up to 25 cycles respectively. For 5 wt.% KCl, it can be seen that the latent heat decreases 5% after 20 cycles from 181 J/g to 170 J/g but remains constant after it. The melting point is also stable after 15 cycles. Findings from the independent additive studies suggest that a combination of 5 wt.% KCl and 2 wt.% of SrCl₂.6H₂O stabilizes the PCM by eliminating the phase separation, suppressing the supercooling and reproducing the congruent melting behavior over a substantial number of cycles. In this formulation, semi congruent melting of the PCM is prevented and the solid and liquid phases are in stable equilibrium at the melting point.

Figure 15 shows the comparison of enthalpy for CaCl.6H₂O without any additives and with KCl at 2, 3 and 5 wt.% and 2 wt.% SrCl₂.6H₂O up to 15 cycles. It can be clearly seen that enthalpy increases on addition of KCl. This shows that KCl also increases the heat storage capacity and the improvement is maintained for the repeated thermal cycles.

Buildings **2022**, 12, 1762 15 of 19

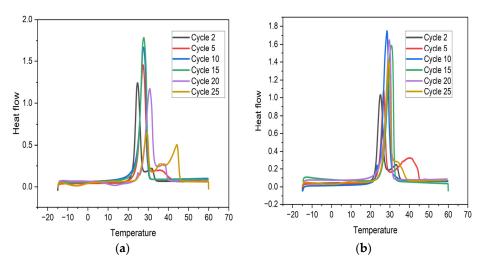


Figure 14. DSC curves for multiple cycles for (a) 3% KCl and 2% SrCl₂.6H₂O; (b) 5% KCl with 2% SrCl₂.6H₂O.

Table 7. Results for 3 wt.% KCl reported through DSC and T-history.

Heating Cycle	T _m (°C)	Peak (°C)	Enthalpy (J/g)	CC4 Formation	Supercooling (°C)
2nd Cycle	22.4	24.6	132	Yes	1.22
5th Cycle	24.6	27.3	183	Yes	11
10th Cycle	25.0	27.8	204	No	1
15th Cycle	25.6	27.6	190	No	No
20th Cycle	26.9	30.7	181	Yes	No
25th Cycle	25.7	29.3	160	Yes	No

Table 8. Results for 5 wt.% KCl reported through DSC and T-history.

Heating Cycle	T _m (°C)	Peak (°C)	Enthalpy (J/g)	CC4 Formation	Supercooling (°C)
2nd Cycle	22.4	25.1	128	Yes	2
5th Cycle	24.4	26.7	178	Yes	5
10th Cycle	25.1	28.4	196	No	5
15th Cycle	26.6	30.8	181	No	1
20th Cycle	26.2	29.68	170	No	No
25th Cycle	26.3	29.3	169	No	No

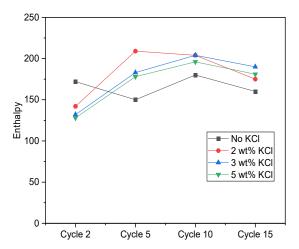


Figure 15. Comparison of latent heat for $CaCl_2.6H_2O$ for 15 cycles without KCl and with KCl (2, 3 and 5%).

Buildings **2022**, 12, 1762 16 of 19

4.4.4. Modification of CaCl₂.6H₂O with NaCl and SrCl₂.6H₂O

Testing of PCM samples containing $SrCl_2.6H_2O$ and 2 or 3 wt.% NaCl showed the two melting peaks indicative of formation of $CaCl_2.4H_2O$, whereas for 5 wt.% NaCl, there was no $CaCl_2.4H_2O$ formation for up to 25 cycles. Further evidence of phase stabilization is shown in Figure 16; for 5 wt.% NaCl, the melting curves were sharp and the melting point of this PCM also was stable. Table 9 shows the latent heat, melting point and the supercooling for 5 wt.% NaCl and 2% $SrCl_2.6H_2O$ up to 25 cycles. The latent heat for cycle 2 is 168 J/g and it increases about 5% after 25 cycles, with no supercooling. Inclusion of both 2% $SrCl_2.6H_2O$ and 5 wt.% of NaCl modifies the semi-congruent behavior of this PCM so that the hexahydrate is no longer converted to lower hydrates.

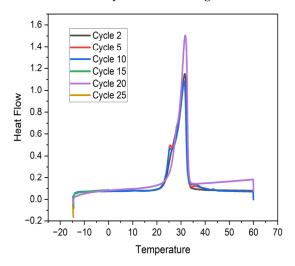


Figure 16. DSC curve for 5 wt.% NaCl and 2 wt.% SrCl₂.6H₂O up to 25 cycles.

Table 9. Results for 5 wt.% NaCl reported through DSC and T-history.

Heating Cycle.	T _m (°C)	Peak (°C)	Enthalpy (J/g)	CC4 Formation	Supercooling (°C)
2nd Cycle	24.5	30	168	No	3
5th Cycle	25.4	29.9	170	No	No
10th Cycle	25.1	29.9	171	No	No
15th Cycle	24.6	30.8	172	No	No
20th Cycle	24.2	29.8	173	No	No
25th Cycle	25.3	30.5	178	No	No

4.4.5. Analysis of XRD Pattern for CaCl₂.6H₂O PCM System

The XRD tests were conducted on the combination of CaCl₂.6H₂O with 5 wt.% KCl/NaCl and 2 wt.% of SrCl₂.6H₂O. Figure 17 shows the XRD pattern comparison for three PCM samples. This comparison was done to see if there were any changes in peak locations due to structural changes in the synthesized PCM. It was found that the peak locations for all three samples were dearly identical, which verifies that there was no chemical reaction of KCl or NaCl and SrCl₂.6H₂O with CaCl₂.6H₂O instead there is only physical interaction. The CaCl₂.6H₂O PCM system with additives behaved similarly to CaCl₂.6H₂O without any additives and had no impact on the crystal structure.

Buildings 2022, 12, 1762 17 of 19

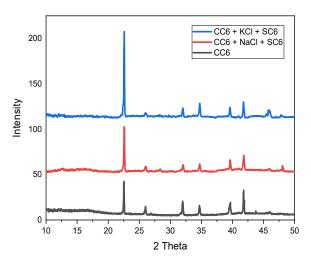


Figure 17. XRD comparison of CaCl₂.6H₂O with and without additives.

5. Conclusions

This publication summarizes the work done on the CaCl₂.6H₂O PCM, which has melting temperature at 25–27 °C and latent heat around 170 J/g, suitable for the building applications. A series of thermal performance tests was conducted to understand the challenges associated with preparing this PCM formulations. This includes the formulation selection and synthesis method, thermal stability and supercooling. Three salt additives were used to form a stable PCM system suitable for thermal cycling. Beginning with the preparation method, the key finding of this research was that no heating is required to prepare the CaCl₂.6H₂O PCM. The use of heating during the PCM preparation may couse the formation of lower hydrates of CaCl₂ and lead to congruent melting behavior. Furthermore, the T-history method test showed increasing supercooling with repeated thermal cycles for CaCl₂.6H₂O from 4 °C to 12 °C after 15 cycles. DSC test results showed that initially CaCl₂.4H₂O was not formed, and latent heat was 172 J/g; however, with increasing number of thermal cycles, latent heat reduced and CaCl₂.4H₂O formation led to two melting peaks. The addition of SrCl₂.6H₂O (2, 3 and 5 wt.%) was able to suppress the supercooling to 1 °C, however together with increasing number of thermal cycles, 3 and 5 wt.% SrCl₂.6H₂O formulations were not able to maintain supercooling at 1 °C, and consequently, the latent heat was reduced. These test demonstrated that 2 wt.% SrCl₂.6H₂O was effective in mitigating the supercooling and maintaining the latent heat of the CaCl₂.6H₂O system. KCl/NaCl were added to encourage congruent melting of this PCM, but neither KCl, nor NaCl were able to prevent supercooling. Lastly, it was shown that the combination of 5 wt.% KCl or NaCl, and with 2 wt.% fixed proportion of SrCl₂.6H₂O resulted in congruent melting with a single melting peak (no formation of CaCl₂.4H₂O), and no supercooling. These results for the combination of 5 wt.% of KCl and NaCl with 2% SrCl₂.6H₂O had latent heat of 169 J/g and 178 J/g and melting temperature of $26 \,^{\circ}$ C and $25 \,^{\circ}$ C up to $25 \,^{\circ}$ C ycles, respectively, which makes it a good choice for commercialization of this PCM in building applications.

Author Contributions: Conceptualization, J.K., M.J.S., P.H. and J.T.; methodology, M.J.S., J.K. and J.T.; formal analysis, J.T. and N.B.; investigation, J.T. and P.H.; resources, J.K., P.H. and M.J.S.; data curation, J.T. and P.H.; writing—original draft preparation, J.T., M.J.S. and J.K.; writing—review and editing, J.T., M.J.S. and A.C.C.; supervision, J.K. and M.J.S.; project administration, J.K.; funding acquisition, J.K. All authors have read and agreed to the published version of the manuscript.

Funding: Research presented in this research was funded by the U.S. Department of Energy grant DE-EE0009156, and the U.S. Navy, Office of Naval Research grant "University—Navy Research Collaboration on Energy Resiliency".

Data Availability Statement: The non-proprietary research data presented in this paper is available from the corresponding author upon the reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Capuano, L. International Energy Outlook 2020 (IEO2020). *U.S. Energy Inf. Adm.* **2020**, 2020, 1–7. Available online: https://www.eia.gov/outlooks/ieo/pdf/ieo2020.pdf (accessed on 8 August 2021).

- 2. Kośny, J. PCM-Enhanced Building Components, an Application of Phase Change Materials in Building Envelopes and Internal Structures; Springer: Cham, Seitzerland, 2015. [CrossRef]
- 3. Cui, Y.; Xie, J.; Liu, J.; Wang, J.; Chen, S. A review on phase change material application in building. *Adv. Mech. Eng.* **2017**, *9*, 1687814017700828. [CrossRef]
- 4. Souayfane, F.; Fardoun, F.; Biwole, P.-H. Phase change materials (PCM) for cooling applications in buildings: A review. *Energy Build.* **2016**, *129*, 396–431. [CrossRef]
- 5. Xie, N.; Huang, Z.; Luo, Z.; Gao, X.; Fang, Y.; Zhang, Z. Inorganic Salt Hydrate for Thermal Energy Storage. *Appl. Sci.* **2017**, 7, 1317. [CrossRef]
- 6. Faraji, H.; Benkaddour, A.; Oudaoui, K.; El Alami, M.; Faraji, M. Emerging applications of phase change materials: A concise review of recent advances. *Heat Transf.* **2021**, *50*, 1443–1493. [CrossRef]
- 7. Sharma, A.; Tyagi, V.V.; Chen, C.R.; Buddhi, D. Review on thermal energy storage with phase change materials and applications. *Renew. Sustain. Energy Rev.* **2009**, *13*, 318–345. [CrossRef]
- 8. Hirschey, J.; Gluesenkamp, K.R.; Mallow, A.; Graham, S. Review of Inorganic Salt Hydrates with Phase Change Temperature in Range of 5–60 °C and Material Cost Comparison with Common Waxes. In Proceedings of the International High Performance Buildings Conference, West Lafayette, IN, USA, 9–12 July 2018; pp. 1–10.
- 9. Abhat, A. Low temperature latent heat thermal energy storage: Heat storage materials. Sol. Energy 1983, 30, 313–332. [CrossRef]
- 10. Naumann, R.; Emons, H.-H. Results of thermal analysis for investigation of salt hydrates as latent heat-storage materials. *J. Therm. Anal.* **1989**, *35*, 1009–1031. [CrossRef]
- 11. Pendyala, S. Macroencapsulation of Phase Change Materials for Thermal Energy Storage. Prog. Mater. Sci. 2014, 65, 67–123.
- Ostrý, M.; Bantová, S.; Struhala, K. Tests on Material Compatibility of Phase Change Materials and Selected Plastics. *Molecules* 2019, 24, 1398. [CrossRef]
- 13. Farrell, A.J.; Norton, B.; Kennedy, D.M. Corrosive effects of salt hydrate phase change materials used with aluminium and copper. *J. Mater. Process. Technol.* **2006**, *175*, 198–205. [CrossRef]
- 14. Mohamed, S.A.; Al-Sulaiman, F.A.; Ibrahim, N.I.; Zahir, H.; Al-Ahmed, A.; Saidur, R.; Yılbaş, B.S.; Sahin, A.Z. A review on current status and challenges of inorganic phase change materials for thermal energy storage systems. *Renew. Sustain. Energy Rev.* **2017**, 70, 1072–1089. [CrossRef]
- 15. Safari, A.; Saidur, R.; Sulaiman, F.; Xu, Y.; Dong, J. A review on supercooling of Phase Change Materials in thermal energy storage systems. *Renew. Sustain. Energy Rev.* **2017**, *70*, 905–919. [CrossRef]
- 16. Beaupere, N.; Soupremanien, U.; Zalewski, L. Nucleation triggering methods in supercooled phase change materials (PCM), a review. *Thermochim. Acta* **2018**, *670*, 184–201. [CrossRef]
- 17. Purohit, B.K.; Sistla, V.S. Inorganic salt hydrate for thermal energy storage application: A review. *Energy Storage* **2021**, *3*, e212. [CrossRef]
- 18. Xin, Y.; Nian, H.; Li, X.; Zhang, B.; Tan, X.; Li, J.; Zhou, Y. Construction of Na₂CO₃·10H₂O-Na₂HPO₄·12H₂O eutectic hydrated salt/NiCo₂O₄-expanded graphite multidimensional phase change material. *J. Energy Storage* **2022**, *52*, 104781. [CrossRef]
- 19. Fang, Y.; Su, J.; Tang, Y.; Liang, X.; Wang, S.; Gao, X.; Zhang, Z. Form-stable Na₂SO₄·10H₂O-Na₂HPO₄ 12H₂O eutectic/hydrophilic fumed silica composite phase change material with low supercooling and low thermal conductivity for indoor thermal comfort improvement. *Int. J. Energy Res.* **2020**, *44*, 3171–3182. [CrossRef]
- 20. Kamidollayev, T.; Trelles, J.P.; Thakkar, J.; Kosny, J. Parametric Study of Panel PCM–Air Heat Exchanger Designs. *Energies* **2022**, 15, 5552. [CrossRef]
- 21. Ye, R.; Lin, W.; Fang, X.; Zhang, Z. A numerical study of building integrated with CaCl₂·6H₂O/expanded graphite composite phase change material. *Appl. Therm. Eng.* **2017**, *126*, 480–488. [CrossRef]
- 22. Schmit, H.; Pfeffer, W.; Rathgeber, C.; Hiebler, S. Calorimetric investigation of the concentration dependent enthalpy change around semicongruent melting CaCl₂·6H₂O. *Thermochim. Acta* **2016**, *635*, 26–33. [CrossRef]
- 23. Feilchenfeld, H.; Fuchs, J.; Sarig, S. A calorimetric investigation of the stability of stagnant calcium chloride hexahydrate melt. *Sol. Energy* **1984**, 32, 779–784. [CrossRef]
- 24. Bo Carlsson, M.; Hans Stynne, S. Method and Apparatus in Storing Heat. U.S. Patent US4466478A, 21 August 1984.
- 25. Feilchenfeld, H.; Sarig, S. Calcium chloride hexahydrate: A phase-changing material for energy storage. *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, 24, 130–133. [CrossRef]
- 26. Arbanas, V.; Bukovec, N.; Bukovec, P. TG and DSC investigation of CaCl₂·6H₂O PCM material. *Thermochim. Acta* 1989, 144, 235–240. [CrossRef]
- 27. Kimura, H.; Kai, J. Phase change stability of CaCl₂·6H₂O. Sol. Energy 1984, 33, 557–563. [CrossRef]
- 28. Tyagi, V.; Buddhi, D. Thermal cycle testing of calcium chloride hexahydrate as a possible PCM for latent heat storage. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 891–899. [CrossRef]

29. Xu, X.; Dong, Z.; Memon, S.A.; Bao, X.; Cui, H. Preparation and Supercooling Modification of Salt Hydrate Phase Change Materials Based on CaCl₂·2H₂O/CaCl₂. *Materials* **2017**, *10*, 691. [CrossRef]

- 30. Xu, X.; Cui, H.; Memon, S.A.; Yang, H.; Tang, W. Development of novel composite PCM for thermal energy storage using CaCl₂·6H₂O with graphene oxide and SrCl₂·6H₂O. *Energy Build.* **2017**, *156*, 163–172. [CrossRef]
- 31. Charles, J.M. Performance and Stability of CaCl₂ 6H₂O-Based Phase Change Materials. Ph.D. Thesis, Lehigh University, Bethleham, PA, USA, 2019. [CrossRef]
- 32. Kurniati, N.; Palittin, I.D.; Sutjahja, I.; Kurnia, D. The Effect of Additives on the Crystallization PCM CaCl₂ 6H₂O for Stabilizing the Air Temperature for Energy Conservation. *Adv. Mater. Res.* **2015**, *1112*, 563–566. [CrossRef]
- 33. Paris, J.; Jolly, R. Observations sur le comportement a la fusion-solidification du chlorure de calcium hexahydrate. *Thermochim. Acta* **1989**, *152*, 271–278. [CrossRef]
- 34. Yinping, Z.; Yi, J. A simple method, the-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials. *Meas. Sci. Technol.* **1999**, *10*, 201–205. [CrossRef]
- 35. McMurdie, H.F.; Morris, M.C.; Evans, E.H.; Paretzkin, B.; de Groot, J.H.; Hubbard, C.R.; Carmel, S.J. Standard x-ray diffraction powder patterns: Section 12, data for 57 substances. In *Interim Report National Bureau of Standards*; National Institute of Standards & Technology Research Information Center: Gaithersburg, MD, USA, 1975.