Experimental Characterization of Low-Temperature Inorganic. Phase Change Materials by Differential Scanning Calorimetry

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Abstract: Recently, phase change materials (PCMs) have received significant attention due to their potential for high-density thermal energy storage. While high-temperature PCMs have received the most focus in the thermal energy storage community, there are potential uses for PCMs with phase transition temperatures close to typical ambient temperatures (15-35°C). For a PCM to be widely used in a large-scale thermal energy storage system, it must meet the cost, safety, and energy density criteria in addition to having an appropriate phase change temperature. Inorganic, hydrated salt PCMs are the most promising, low-temperature PCMs, which can meet all of these criteria. After completing a review of known inorganic PCMs with phase change temperatures in the desired range, six of the more promising PCMs were tested by differential scanning calorimetry (DSC) to determine both their phase change temperatures (T_m) and latent heats of fusion (H_f). The first of these PCMs (potassium fluoride tetrahydrate) was eliminated after successful DSC testing as it became apparent that this PCM had serious health and safety concerns. Two new calcium chloride hexahydrate ($CaCl_2{\cdot}6H_2O$)-based PCMs were also tested: $CaCl_2{\cdot}6H_2O$ + potassium nitrate (KNO_3) and $CaCl_2{\cdot}6H_2O$ + magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$). For $CaCl_2{\cdot}6H_2O + KNO_3$, it was found that the melt temperature of the PCM could be varied by changing the percentage of KNO_3. In the case of the $CaCl_2{\cdot}6H_2O$ + $MgCl_2{\cdot}6H_2O$, phase diagram modeling and physical experiments were used to determine the correct eutectic mixture, which leads to congruent melting/freezing of this PCM. $CaCl_2{\cdot}6H_2O$ was also tested by DSC, with found T_m and H_f results similar to those presented in the literature. Finally, sodium sulfate decahydrate ($Na_2SO_4{\cdot}10H_2O$) and $Na_2SO_4{\cdot}10H_2O$ + 25 wt% H_2O were tested by DSC. For both of these PCMs, significant phase separation was observed, which must be addressed if these PCMs are to be used commercially.

Keywords: Latent energy storage, Phase change material, Energy storage, Hydrated salt, Calcium chloride hexahydrate, PCM.

INTRODUCTION

Thermal energy storage has been utilized by mankind for millennia. Most historic thermal energy storage techniques are based on sensible thermal energy storage – with one notable exception – the latent thermal energy transfer accompanying the melting or freezing of water. The high energy density of this phase change has made ice very useful for cooling everything, from drinks to early refrigerators. More recently, materials with a high solid/liquid phase change temperature (> 300°C) have begun to be used for storing thermal energy that is captured in large solar thermal power plants. In the late 1970's and 1980's, several researchers considered low-temperature phase change materials (PCMs) primarily for use in temperature regulation of buildings. This work was conducted by researchers such as Telkes [1], Lane [2,3], Carlsson [4], Abhat [5], and Kimura, [6-8] with their work forming the bulk of the seminal research into low-temperature PCMs. After little low-temperature PCM work in the 1990's and early 2000's, interest in the topic was renewed in the later years of the first decade of the 21st century. Since then many papers have been published on the topic by the likes of N'Tsoukpoe [9,10], Tyagi [11,12], Carlsson [13], Sharma [14-16], and Oró [17] among others.

While there are numerous organic and inorganic low-temperature PCMs, inorganic hydrated salt PCMs are of particular interest due to their low cost and wide availability. The low-temperature PCM application considered in this paper is the use of a PCM for daytime supplemental cooling of main steam-condensers in power plants. The proposed system is illustrated in Figure **1**. In this system, sealed trays of PCM are stacked vertically around centrally-located thermosyphons, which move thermal energy into and out of the PCM. During the day, hot steam from the last steam turbine stage is distributed to the bottoms of the thermosyphons in a manifold. Thermal energy from the steam is transferred to the PCM through the thermosyphons, where it melts the PCM. This system would be particularly beneficial for a power plant, which uses dry cooling (an air-cooled condenser) as the performance of these plants suffer on hot days, when thermal energy cannot be transferred efficiently to the air. By transferring the thermal energy from the steam into the PCM during melting, steam from the turbine is condensed at a lower temperature, which improves steam turbine power output. During the night, the PCM is frozen as thermal energy from the PCM is

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E-ISSN: 2409-5826/19

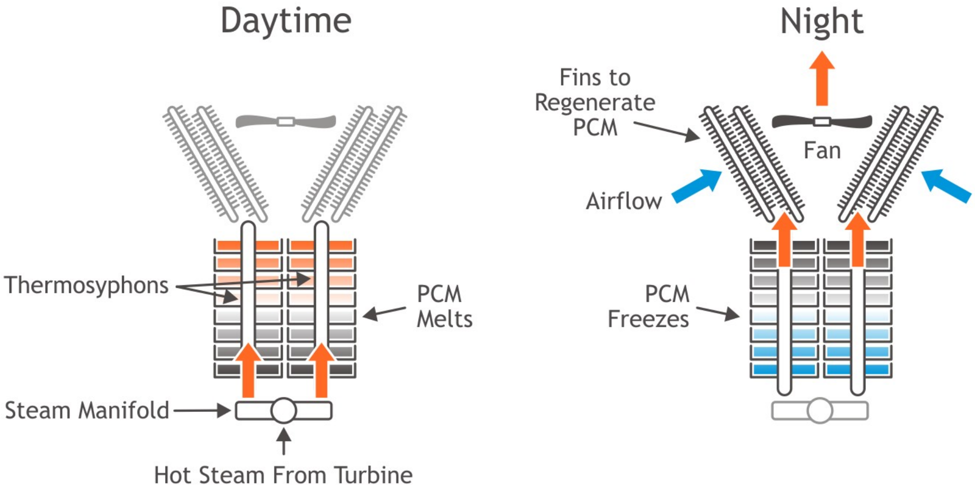

Figure 1: Proposed PCM Cold Storage System for Power Plant Condenser Cooling.

transferred up the thermosyphons and rejected to the now cooler ambient air. It has been determined that a PCM with a phase change temperature (T_m) of between 15 and 35°C is optimum for this application. The precise value of T_m for a given condenser is location specific, as it depends on the local day and night air temperatures.

PCM Selection

Selection of an appropriate PCM is highly dependent on the application for which it will be used. For the case of a PCM-cooled steam condenser, it was determined that T_m, PCM cost, latent heat of fusion (H_f), long-term PCM stability, and health and safety were the primary selection criteria. A failure to meet the required condition for any of these primary selection criteria would be sufficient to disqualify a PCM. The following PCM secondary selection criteria were also considered: corrosivity, thermal conductivity, energy density, and any encapsulation requirements. While a failure to meet these criteria would not necessary eliminate the material from consideration, the implications of failing to meet the criteria would need to be addressed if the PCM were to be used in the proposed system.

In the required phase change temperature range of between 15°C and 35°C, there are three major groups of PCMs which have been widely studied; organic paraffin waxes, fatty acids and inorganic hydrated salts. Each of these groups have specific advantages and disadvantages. Figure **2** presents H_f vs. cost for these three groups of PCMs. It can be seen that all three groups can have similar H_f values (although the fatty acids are generally lower). However, as seen, some hydrates salts can be an order of magnitude less expensive than the least expensive organic PCMs. This cost advantage is important for large systems such as the proposed condenser cooling system, where the required quantities of PCM can easily exceed tens of tons. A comprehensive review of hydrated salt PCMs, with a phase change temperature of between 15 and 35°C, was conducted with a list of found PCMs, presented in Table **1**. The potential list of hydrated salt PCMs is expanded considerably if mixtures of salts are considered. Typically, these mixtures are prepared such that they have more desirable properties than either of the parent salts forming the mixture. A list of hydrated salt mixtures and eutectics, with melting temperatures between 15 and 35°C, is presented in Table **2**.

Although all of the PCMs presented in Tables **1** and **2** are hydrated salts, their price can still vary by as

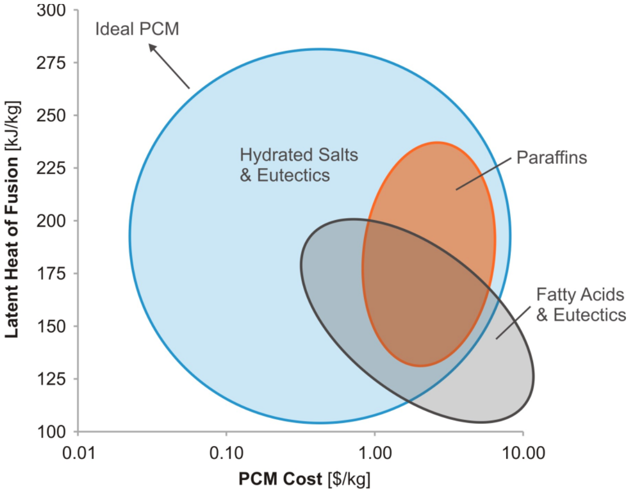

Figure 2: PCM Groups with Phase Change Temperatures Between 15 & 35°C.

Table 1: Salt Hydrate Inorganic PCMs in the Temperature Range of Interest

Hydrated Salts	[°C] T_m	[kJ/kg] H_f	[kJ/kg°C] Cp_L	[kJ/kg°C] Cp_S	[kg/m3] d_L	[kg/m3] d_S	[W/m°C] k_L	[W/m°C] k_T	[W/m°C] k_S	Sources
$NaOH\cdot 3.5H_2O$*	15.0 - 15.5	219								[20-24]
$Na_2CrO_4\cdot 10H_2O$	18									[20, 24]
$KF\cdot 4H_2O$*	18.0 - 20.0	230 - 246	2.39 - 2.47	1.62 - 1.84	1447 - 1456	1437 - 1455	0.479		0.608	[22, 25-27]
$LiClO_4\cdot 3H_2O$	20									[28]
$FeBr_3\cdot 6H_2O$	21.0 - 27.0	105								[15]
$Mn(NO_3)_2\cdot 6H_2O$	25.0 - 26.0	126 - 148			1728	1600 - 1795				[12, 15, 24, 27, 29-32]
$LiBO_2\cdot 8H_2O$	25.7	289								[33]
$CaCl_2\cdot 6H_2O$*	27.0 - 29.9	160 - 201	2.13 - 2.32	1.44 - 1.46	1496 - 1562	1690 - 1802	0.539 - 0.561	0.7	1.09 - 1.10	[3-5, 22, 25, 29, 33-39]
$Na_2HAsO_4\cdot 12H_2O$	28					1736				[36]
$LiNO_3\cdot 3H_2O$	29.9 - 30.2	189 - 296	2.76	1.73	1425 - 1430	1550 - 1575	0.584		0.82	[15, 25, 36, 40]
$Na_2SO_4\cdot 10H_2O$*	31.1 - 32.5	222 - 254	3.26 - 3.31	1.76 - 1.93	1330 - 1410	1458 - 1485	0.544 - 0.589		0.514	[1, 3, 15, 18, 22, 28, 36, 39, 41-47]
$Na_2CO_3\cdot 10H_2O$	32.0 - 36.0	247 - 267				1440 - 1442				[15, 22, 25, 36, 39]
$KFe(SO_4)_2\cdot 12H_2O$	33	173								[15]
$CaBr_2\cdot 6H_2O$	34	116 - 138			1956	2194				[3, 15, 22, 27]
$LiBr_2\cdot 2H_2O$	34	124								[15]
$Na_2HPO_4\cdot 12H_2O$	35.0 - 36.1	279 - 280	1.93 - 2.51	1.55 - 1.68		1552 - 1520	0.589		2.93	[25, 38, 46]

*Tested by DSC.

Table 2: Salt Hydrate PCMs Mixtures in the Temperature Range of Interest

Hydrated Salt Mixtures			Type	[°C] T_m	[kJ/kg] H_f	[J/g°C] Cp_L	[J/g°C] Cp_S	[kg/m^3] d_L	[kg/m^3] d_S	Sources
$Mn(NO_3)_2 \cdot 6H_2O$ (96%)	$MnCl_2 \cdot 4H_2O$ (4%)		wt%	15.0 - 25.0	126	2.78	2.34	1728 - 1738	1795	[21, 48]
$Mn(NO_3)_2 \cdot 6H_2O$ (99%)	$MnCl_2 \cdot 4H_2O$ (1%)		wt%	22.1	121					[32]
$Cu(NO_3)_3 \cdot 6H_2O$ (51-55%)	$LiNO_3 \cdot 3H_2O$ (49-45%)		wt%	16.5	250					[28]
$LiNO_3 \cdot 3H_2O$ (52-45%)	$Zn(NO_3)_2 \cdot 6H_2O$ (48-55%)		wt%	17.2	220					[21, 28]
$Na_2SO_4 \cdot 10H_2O$ (50%)	NaCl (50%)		mol %	18	286	3.26	1.76			[32, 49]
$CaCl_2 \cdot 6H_2O$ (82%)	$MgCl_2 \cdot 6H_2O$ (18%)*		wt%	21.9						
$CaCl_2 \cdot 6H_2O$ (66.6%)	$MgCl_2 \cdot 6H_2O$ (33.3%)*		wt%	23.0 - 25.0	127	2.74		1590		[25, 29, 50]
$CaCl_2 \cdot 6H_2O$ (50%)	$MgCl_2 \cdot 6H_2O$ (50%)*		wt%	25	95					[15]
$Co(NO_3)_2 \cdot 6H_2O$ (41.5-52.5%)	$LiNO_3 \cdot 3H_2O$ (37.8-52.7%)	H2O (5.8-9.7%)	wt%	22.3	265					[28]
$CaCl_2 \cdot 6H_2O$ (95%)	$Mg(NO_3)_2 \cdot 6H_2O$ (5%)		wt%	22.8	162	2.74	3.54		1481	[51]
$Na_2SO_4 \cdot 10H_2O$ (75.1%)	H_2O (24.9%)*		wt%	24	159					[28]
$Na_2SO_4 \cdot 10H_2O$ (79.9%)	H_2O (20.1%)		wt%	27	178					[28]
$Na_2SO_4 \cdot 10H_2O$ (84.9%)	H_2O (15.1%)		wt%	29	199					[28]
$Na_2SO_4 \cdot 10H_2O$ (90.4%)	H_2O (9.6%)		wt%	32	214					[28]
$Na_2SO_4 \cdot 10H_2O$ (94.7%)	H_2O (5.3%)		wt%	32	237					[28]
$LiNO_3 \cdot 3H_2O$ (65-55%)	$Ni(NO_3)_2 \cdot 6H_2O$ (35-45%)		wt%	24.2	230					[28]
$Ca(NO_3)_2 \cdot 6H_2O$ (45%)	$Zn(NO_3)_2 \cdot 6H_2O$ (55%)		wt%	25	130			1931		[52]
$Ca(NO_3)_2 \cdot 4H_2O$ (47%)	$Mg(NO_3)_2 \cdot 6H_2O$ (53%)		wt%	30	134 - 136					[15, 53]
$Ca(NO_3)_2 \cdot 4H_2O$ (67%)	$Mg(NO_3)_2 \cdot 6H_2O$ (33%)		wt%	30	136			1676		[52]
$Ca(NO_3)_2 \cdot 4H_2O$ (72%)	$Al(NO_3)_3 \cdot 9H_2O$ (28%)		wt%	35	139			1727		[52]
$CaCl_2 \cdot 6H_2O$ (93%)	KNO_3 (7%)*		wt%	25	120					
$CaCl_2 \cdot 6H_2O$ (95.3%)	NaCl (4.3%)	KCl (0.4%)	wt%	26.0 - 26.8	188 - 189	1.44	1.35		1640	[5, 33, 25, 46]
$Mg(NO_3)_2 \cdot 6H_2O$ (18%)	$Zn(NO_3)_2 \cdot 6H_2O$ (82%)		wt%	32	130			1915		[52]

*Tested by DSC.

much as two orders of magnitude, as seen in Figure **2**. After a thorough cost analysis, only those PCMs with the highest latent heat to cost ratio were selected to be chracterized using differential scanning calorimetry (DSC).

DSC Testing Procedure

A TA Q2000 DSC (temperature accuracy ± 0.1°C, calorimetric reproducibility ± 0.05%) was used to characterize the selected PCMs. 15 to 25 mg samples placed into hermetically sealed, aluminum pans were individually loaded into the DSC using an autosampler. Nitrogen was used as a purge gas at a flow rate of 50 mL/min. A standardized DSC test regime was followed for all samples. After equalizing each sample at -30°C to ensure complete freezing, the samples were heated to 50°C at a heating rate of 7°C/min. After reaching 50°C, the samples were cooled to -20°C at the same rate. Since the DSC records the energy balance of the sample during heating and cooling, the heat flux per unit time can be used to measure both, the phase change temperature and heat released or gained, during the phase change. Figure **3** presents an example of the DSC melting curve for a hydrated salt PCM and how it is used to find T_m and H_f. As the PCM is melted, a large release of heat relative to a small temperature change results in a peak in the heat flux curve. The temperature at the tip of this peak (point of maximum heat flux) is refered to as the peak temperature (T_p). While some researchers refer to T_p as the melting temperature of the PCM, our research has uncovered a second method which more accurately predicts the melting temperature. First, a line is drawn tangent to the steepest portion of the curve to the left of T_p. The temperature corresponding to the point where this line intersects with a line drawn across the bottom of the peak is refered to as the onset temperature (T_o). In order to determine if T_o or T_p is a better approximation of the melting temperature, larger (10-50g) PCM samples were fitted with resistance temperature detectors (RTDs) and melted in a water bath. Upon examination of the RTD temperature trace, the melting temperature was clearly seen as it corresponds with the point where the temperature curve flattens. Using this method, it was consistently found that the DSC onset temperature was a better approximation of the melting temperature than the peak temperature. H_f is determined from the DSC test results by computing the area inclosed by the peak and the line drawn across its base; i.e. the blue, shaded region of Figure **3**.

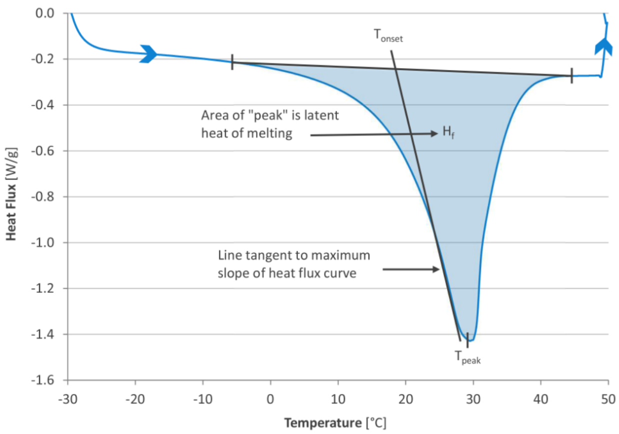

Figure 3: DSC Melting Curve Example.

For all hydrated salt DSC tests, the melting process was used in determining thermal performance of the PCM. The reason for this is that most hydrated salt PCMs experience significant supercooling. Supercooling (also called subcooling or undercooling) is a phenomenon experienced by a freezing PCM, where the temperature must be lowered well below the freezing temperature before crystallization begins. As the temperature is decreased down to the supercooling temperature, the hydrated salt will remain in the liquid state. When the PCM supercools to a temperature sufficiently below the phase change temperature, freezing will eventually begin. This temperature, at which initial nucleation and freezing occurs, is referred to as the supercooling temperature.

Supercooling during a DSC test is illustrated in Figure **4**, where both the heating and cooling portions of the test are shown. After reaching 50°C, the PCM cools with virtually 0 heat flux until it reaches -10°C. Suddenly, the heat flux curve rises vertically before looping due to a rise in the temperature of the sample. This temperature rise during cooling is due the fact that a supercooled sample tends to freeze very quickly, releasing its latent heat of freezing nearly instantaneously. This rapid heat release momentarily overwhelms the cooling capacity of the DSC, resulting in the heat flux loop as seen in Figure **4**.

Although some authors have attempted to use the DSC to study supercooling, they suggest that the results be used with caution as the DSC is known to overpredict supercooling of PCMs [18]. This was found to be case in the present work, with the DSC results overpredicting supercooling by 50 – 100%. It is believed the primary factors driving this overprediction are the high cooling rates of the DSC and the small DSC sample size – an observation reported by Cantor [19].

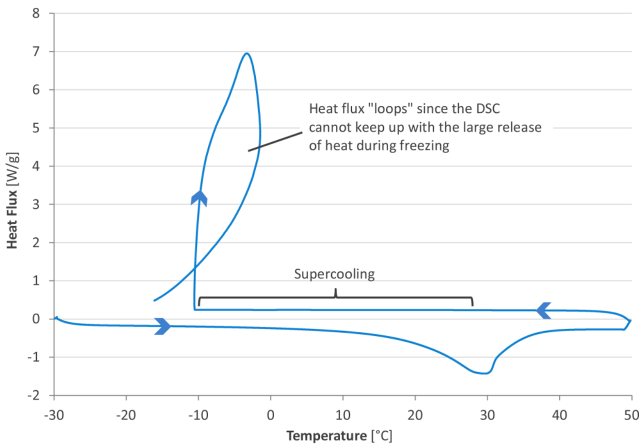

Figure 4: Melting and Freezing DSC Curve Example.

Overview of DSC Test Results

DSC tests were conducted for the selected PCMs, as shown in Table **1** and **2** (denoted by *). For each PCM, the DSC-predicted melt temperature (T_m) and H_f were compared with the literature values in Table **3**. The DSC test results, for most of the PMCs, show good agreement with published values. It should be noted that the performance of several PCMs deviated from that presented in the literature. For instance, DSC testing of sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$) + 25 wt% H_2O found this PCM to have a higher melt temperature than previously reported. Sodium hydroxide 3.5 H_2O ($NaOH \cdot 3.5H_2O$) is not presented in Table **3** as significant issues were encountered during DSC testing; namely a strong exothermic reaction between this PCM and the aluminum sample pan introduced significant errors into the DSC results. The calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) – based PCMs with 7% potassium nitrate (KNO_3) and 18% magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) are novel PCM mixtures, which will be discussed in the following sections.

$KF \cdot 4H_2O$

Potassium fluoride tetrahydrate ($KF \cdot 4H_2O$) is a congruently melting PCM with a melt temperature of 18°C and a very high heat of fusion in excess of 200 J/g. There were safety concerns surrounding the use of potassium fluoride, as it has a moderately high rating of a Category 3 in oral, inhalation, and dermal toxicity, according to the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200) [54]. Despite these concerns, it was decided to test this material using DSC. A DSC melt curve of $KF \cdot 4H_2O$ is presented in Figure **5**.

DSC testing found a T_m = 18°C and high H_f = 213 J/g for $KF \cdot 4H_2O$. In addition to these good values, this salt was observed to melt and freeze congruently. During cooling, $KF \cdot 4H_2O$ was found to supercool considerably, a fact which needs to be addressed before this salt can be used as a viable PCM. While DSC testing of $KF \cdot 4H_2O$ revealed a thermally promising PCM, additional testing of this material was discontinued due to safety concerns. The most notable concern was that fluoride ions are known react with hydrogen ions introduced through the addition of water – forming hydrofluoric acid. Hydrofluoric acid is extremely hazardous with Class 1 and 2 toxicity, according to the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200) [54].

$CaCl_2 \cdot 6H_2O + KNO_3$

During DSC testing of PCMs within the required transition temperature range, a novel PCM mixture was formulated and researched. It was found that the addition of a small quantity of KNO_3 to $CaCl_2 \cdot 6H_2O$ would lower the phase change temperature of $CaCl_2 \cdot 6H_2O$, while still resulting in a congruently melting/freezing PCM. While this PCM has not been characterized or tested in the literature, a similar

Table 3: Summary of DSC Results and Comparison with Published Values

PCM	Literature		DSC Results	
	T_m [°C]	H_f [J/g]	T_m [°C]	H_f [J/g]
$KF \cdot 4H_2O$	18.0 - 20.0	230 - 246	18.0	211
$CaCl_2 \cdot 6H_2O$ + 7% KNO_3	-	-	19.6	120
$CaCl_2 \cdot 6H_2O$ + 18% $MgCl_2 \cdot 6H_2O$	-	-	21.9	149
$CaCl_2 \cdot 6H_2O$ + 33% $MgCl_2 \cdot 6H_2O$	23.0 - 25.0	127	22.8	109
$CaCl_2 \cdot 6H_2O$	27.0 - 29.9	160 - 201	29.1	175
$Na_2SO_4 \cdot 10H_2O$ + 25% H_2O	24.0	159	30.7	175
$Na_2SO_4 \cdot 10H_2O$	31.1 - 32.5	222 - 254	33.2	191

composition is mentioned in a Chinese patent [55]. The motivation behind this PCM formulation was to produce a PCM with a phase transition temperature closer to 25°C than $CaCl_2{\cdot}6H_2O$, which melts at 29°C.

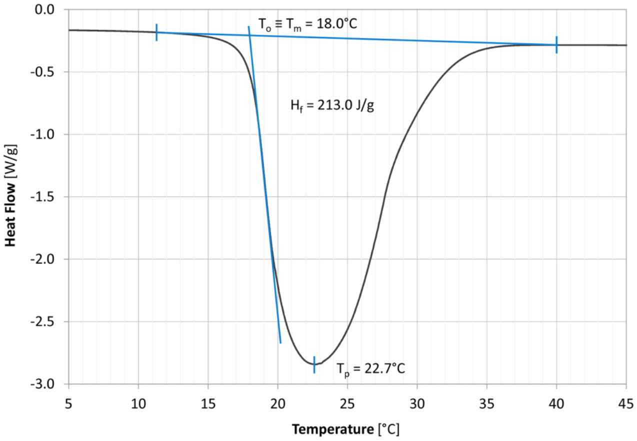

Figure 5: DSC Melting Curve of $KF{\cdot}4H_2O$.

Samples of $CaCl_2{\cdot}6H_2O + KNO_3$ were prepared with between 3.6 and 10.8 wt% KNO_3. These samples were DSC tested with differences in T_m and H_f recorded. Several of these DSC curves are plotted alongside the curve for $CaCl_2{\cdot}6H_2O$ (0 wt% KNO_3) in Figure **6**. It was found that as the concentration of KNO_3 increased, both the melting temperature and the latent heat of melting decreased. Note that a decrease in H_f corresponds to a reduction in the endothermic peak height in Figure **6**. A decrease in T_m is beneficial if a PCM with a slightly lower phase transition temperature is desired. However, this decrease in temperature comes at the cost of PCM thermal storage potential. The change in $CaCl_2{\cdot}6H_2O + KNO_3$ thermal properties with varying KNO_3 percentage is quantified in Table **4**. For the purposes of the proposed steam condenser cooling system, a weight ratio of 93:7 $CaCl_2{\cdot}6H_2O$ to KNO_3 was selected for further testing. At this concentration, T_m = 19.6°C and H_f = 120 J/g.

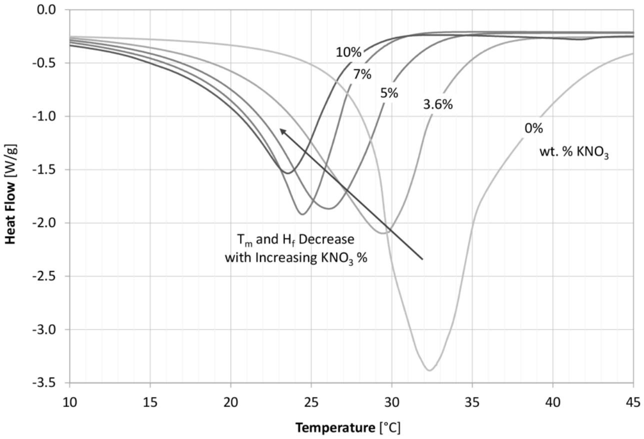

Figure 6: Change in $CaCl_2{\cdot}6H_2O + KNO_3$ Curves with Varying KNO_3 Concentration.

Table 4: DSC Results for Varying Mixtures of $CaCl_2{\cdot}6H_2O + KNO_3$

$CaCl_2{\cdot}6H_2O + KNO_3$ [wt ratio]	T_m [°C]	T_p [°C]	H_f [J/g]
89.2:10.8	15.3	25.3	104.1
90:10	17.3	23.5	97.9
93:7*	19.6	24.5	120.0
93.6:6.4	19.4	27.1	131.4
95:5	19.3	26.1	134.5
96.4:3.6	20.4	29.5	149.4
100:0	28.3	32.3	163.1

*Selected for further characterization.

$CaCl_2{\cdot}6H_2O + MgCl_2{\cdot}6H_2O$

The mixture of $CaCl_2{\cdot}6H_2O$ and $MgCl_2{\cdot}6H_2O$ is a widely discussed PCM in the literature [25, 29, 50]. Typically, a weight ratio of 66:33 $CaCl_2{\cdot}6H_2O$ to $MgCl_2{\cdot}6H_2O$ is stated to be the eutectic mixture of these two salts. The eutectic mixture of two salts is the mixture composition where both salts melt and freeze at the same temperature, with both phases simultaneously undergoing the phase transition. This point corresponds to the lowest melting temperature across the range of possible mixture percentages. While the DSC tests with 66:33 $CaCl_2{\cdot}6H_2O + MgCl_2{\cdot}6H_2O$ showed good agreement with those presented in the literature (see Table **3**), visual observation of larger test samples found that this PCM did not melt and freeze congruently. When frozen to a temperature slightly below the phase transition temperature, a percentage of the PCM was found to remain liquid. Likewise, after melting to a temperature in slight excess of T_m, a portion of the PCM was found to remain solid. Because of these incongruent phase transitions, it was concluded that the 66:33 weight ratio of $CaCl_2{\cdot}6H_2O$ to $MgCl_2{\cdot}6H_2O$ does not correspond to a eutectic mixture of these salts.

With the eutectic mixture of $CaCl_2{\cdot}6H_2O + MgCl_2{\cdot}6H_2O$ unknown, various mixture percentages of the two salts were prepared and visually observed for congruent melting/freezing. If heated to a temperature slightly above the melting temperature or cooled to a temperature slightly below the freezing temperature, a congruently melting/freezing PCM will be observed to be entirely melted or frozen, respectively. At $CaCl_2 \cdot 6H_2O$ concentrations below 82 wt%, a portion of the PCM was found to remain crystallized after the PCM was melted to a temperature slightly above its melt temperature. If the $CaCl_2 \cdot 6H_2O$ concentration was greater than 82 wt%, a liquid layer would form on top of the frozen solid when cooled to slightly below the freezing temperature. If the weight ratio of $CaCl_2 \cdot 6H_2O$ to $MgCl_2 \cdot 6H_2O$ was 82:18, the PCM was observed to melt and freeze congruently.

Given the differences in $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ eutectic concentration suggested by the literature and that found experimentally, phase diagrams for this salt system were modeled. A software packagem developed by Kaj Thomsen, was used to model the phase diagrams [56]. Thomsen's model utilizes the extended UNIQUAC method to calculate the phase equilibria of various electrolyte solutions. The Extended UNIQUAC model is based on excess Gibbs energy, with an added Debye-Hückel law term and a term corresponding to the UNIQUAC equation. More information about this model can be found in work done by Thomsen *et al*. [57] and Iliuta *et al*. [58]. Thomsen's software package allows for modeling of binary, ternary, and quaternary phase diagrams of aqueous salt solutions. The program includes ions for Na^+, H^+, Cl^-, Ca^{2+}, Mg^{2+}, and OH^- among others and is primarily designed for use in oil field and geothermal applications.

First, Thomsen's model was used to model a binary phase diagram of the $CaCl_2 \cdot 6H_2O$-$MgCl_2 \cdot 6H_2O$ system (Figure **7**). Figure **7** shows that at low $MgCl_2 \cdot 6H_2O$ concentrations, the $CaCl_2 \cdot 6H_2O$ phase dominates. At around 15 wt% $MgCl_2 \cdot 6H_2O$, the $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$ phase forms a eutectic mixture with the $CaCl_2 \cdot 6H_2O$ phase. This suggests that the eutectic mixture is very close to the 18 wt% $MgCl_2 \cdot 6H_2O$ composition, as indicated by experimental testing. This finding lends credibility to the suggestion that 82:18 is the eutectic weight ratio for the $CaCl_2 \cdot 6H_2O$+$MgCl_2 \cdot 6H_2O$ PCM mixture.

A ternary $CaCl_2$-$MgCl_2$-H_2O phase diagram was also modeled using Thomson's program (Figure **8**). The primary liquidous curves for four equilibrium temperatures (20, 25, 27, and 30°C) were calculated and plotted. Eutectic concentrations at each temperature are denoted by the inflection points (corners) in these curves. The locations of both, the commonly-assumed eutectic weight ratio of 66:33 and the suggested eutectic mixture of 82:18 $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$, are noted by the open, blue circles in Figure **8**.

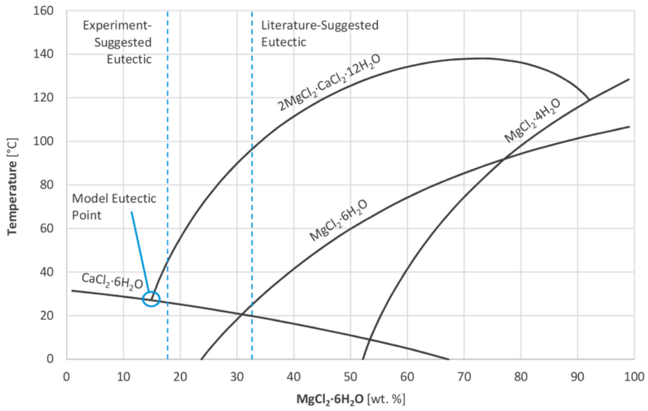

Figure 7: Modeled Binary Phase Diagram of the $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ System.

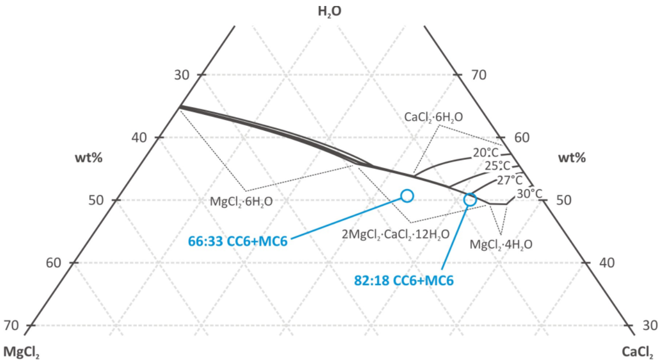

Figure 8: Modeled Ternary Phase Diagram of the $CaCl_2$-$MgCl_2$-H_2O System.

The ternary phase diagram of the $CaCl_2$-$MgCl_2$-H_2O system in Figure **8** clearly shows that the literature-suggested eutectic of 66:33 $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ lies beneath the liquidous curve of the $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$ phase. This changes when the newly-suggested eutectic of 82:18 is considered. It can be seen that this $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ mixture lies very close to a eutectic point formed between the $CaCl_2 \cdot 6H_2O$ and $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$ phases at a temperature of 27°C. Because of the agreement between experimental observation and the modeled phase diagrams of the $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ system, a weight ratio of 82:18 $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ is proposed as the eutectic mixture of these two hydrated salts.

With the correct eutectic mixture of $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ found, DSC testing of this salt was conducted to determine both its T_m and H_f. The DSC melting heat flux curve for this PCM is presented in Figure **9**. DSC testing revealed a T_m = 21.9°C and H_f = 149.2 J/g for the 82:18 $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$ PCM. While this melt temperature is slightly below that suggested in the literature for the 66:33 mixture, the latent heat of fusion is significantly greater, which is beneficial from a heat storage capacity standpoint. No attempt to characterize the supercooling of this PCM using DSC was made given the drawbacks of this method, as outlined previously.

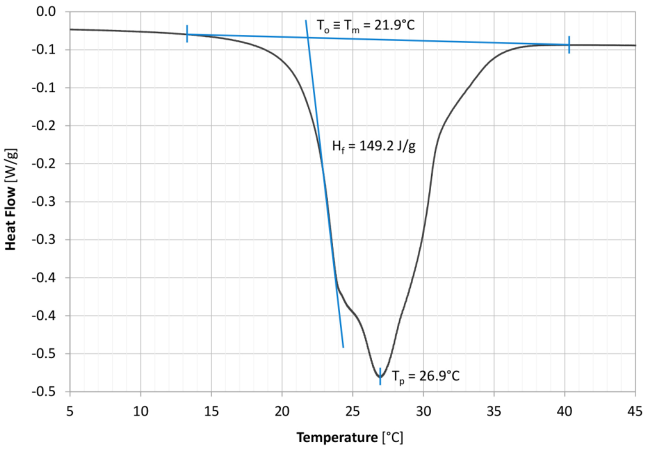

Figure 9: DSC Melting Curve of 82:18 wt. Ratio of $CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$.

$CaCl_2 \cdot 6H_2O$

Calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) is perhaps the most widely studied hydrated salt PCM with a phase transition temperature in the 30°C range. Initial work into this PCM dates back to the 19th century with Roozeboom considering the hydrates of calcium in 1889 [59]. In Hale *et al*'s. work for NASA in the 1970's, $CaCl_2 \cdot 6H_2O$'s melt temperature and latent heat of fusion were recorded [36]. In 1975, Telkes [39] and Lorsch *et al*. [38] touched on $CaCl_2 \cdot 6H_2O$ as a promising hydrated salt PCM, although there was little discussion on any of the challenges associated with its use. Carlsson *et al*'s work in 1979 represents the first work considering the phase stability and/or modification of $CaCl_2 \cdot 6H_2O$ to ensure long-term thermal performance [4]. Phase stability (or separation) refers to the tendency of a PCM to separate into distinct material phases during thermal cycling. If this separation is not reversible, the PCM will lose thermal storage capacity with an increasing number of cycles. During the 1980's, the first detailed work into $CaCl_2 \cdot 6H_2O$ was conducted. Abhat conducted DSC testing of $CaCl_2 \cdot 6H_2O$ [5]. Feilchenfeld *et al*. experimented with $CaCl_2 \cdot 6H_2O$ thickening and the extra-water principle in order to promote phase stability [60]. Also considered by Feilchenfeld *et al*. was the impact of additives, such as KCl, on reducing $CaCl_2 \cdot 6H_2O$'s melt temperature [35,61]. Brandstetter outlined the reasons for phase instability in $CaCl_2 \cdot 6H_2O$ alongside a potential solution in the extra water principle [62]. Perhaps the most seminal work of the period was conducted by George Lane. While working as a researcher at Dow Chemical, Lane considered the addition of $SrCl_2 \cdot 6H_2O$ and other additives to $CaCl_2 \cdot 6H_2O$ as nucleating and stabilization agents [63,64]. In addition, Lane *et al*. found that the addition of small quantities of KCl and NaCl could have a positive impact on $CaCl_2 \cdot 6H_2O$'s phase stability [53,64]. After 1990, work by Heckenkamp *et al*. [25], Esen *et al*. [34], Shahbaz *et al*. [65], and Carlsson [13] expanded the knowledge-base for this PCM. More recently, researchers such as Yuan *et al*. [66] and Li *et al*. [67] have considered the addition of expanded graphite and nanoparticles to $CaCl_2 \cdot 6H_2O$ in order to improve both supercooling, stability, and thermal conductivity.

Several $CaCl_2 \cdot 6H_2O$ samples were tested by DSC to find their melt temperature and heat of fusion. A typical DSC melting test of $CaCl_2 \cdot 6H_2O$ is presented in Figure **10**. For this test, $CaCl_2 \cdot 6H_2O$ was found to melt at 28.1°C with a latent heat of fusion of 187.1 J/g. These values compare well with the literature, although the measured T_m value is below the average literature value, while H_f is slightly greater. A summary of $CaCl_2 \cdot 6H_2O$ DSC thermal results is presented in Table **5**.

Table 5: Summary of DSC Test Results for $CaCl_2 \cdot 6H_2O$

T_m [°C]	T_p [°C]	H_f [J/g]
28.1 – 28.8	32.3 – 33.7	163.1 – 199.5

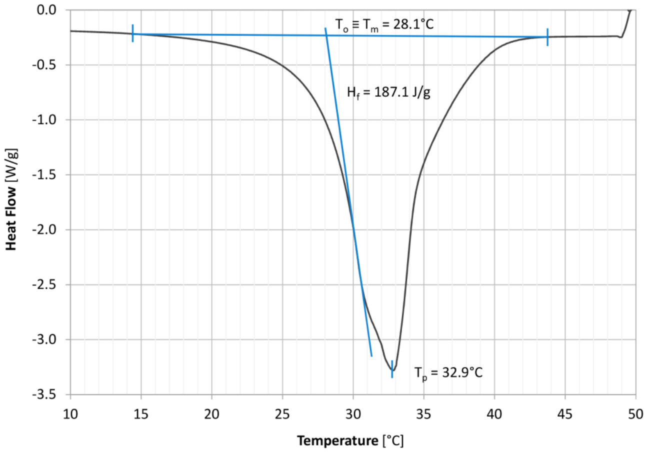

Figure 10: DSC Melting Curve of $CaCl_2 \cdot 6H_2O$.

$Na_2SO_4{\cdot}10H_2O$

Sodium sulfate decahydrate ($Na_2SO_4{\cdot}10H_2O$), also known as Glauber's Salt, is another widely-studied low-temperature PCM. The history of this PCM goes back to the late 1800's with notable early researchers being Cohen [68] and Leenhardt *et al*. [69]. In 1935, Kobe *et al*. published their own thermal research into this material, presenting it alongside previously published results [70]. By 1948, Telkes *et al*. had constructed a solar heated house in Dover, Massachusetts utilizing $Na_2SO_4{\cdot}10H_2O$ as a thermal storage medium [71]. Initial results from this project were promising. However, as later related by Butti *et al*., by the third winter the salt had deteriorated and separated into two distinct layers, one remaining liquid while the other was solid [72]. Telkes continued to experiment with $Na_2SO_4{\cdot}10H_2O$, finding that this PCM contains 44% anhydrous Na_2SO_4 with the remainder being H_2O by weight. At the phase transition temperature of 32.4°C, approximately 85 wt% of the PCM forms a saturated solution with the water as $Na_2SO_4{\cdot}10H_2O$, while the remaining 15% remains in the solid, anhydrous form, settling at the bottom of the container due to the higher density of the anhydrous solid. To prevent this phase separation, Telkes introduced thickening agents, such as wood pulp or silica gel, which prevented the anhydrous solid from settling out of the $Na_2SO_4{\cdot}10H_2O$ solution. This thickened $Na_2SO_4{\cdot}10H_2O$ was cycled 1,000 times without a significant change in thermal performance being observed [39].

$Na_2SO_4{\cdot}10H_2O$ was tested by DSC to find its melt temperature and latent heat of melting (Figure **11**). The measured T_m of 33.2°C is slightly above that presented in the literature, while the measured H_f of 190.6 J/g is considerably lower than the published data. Upon examination of the melting curve in Figure **11**, it is apparent that a second melting peak occurs at -0.7°C. Since this salt is known to disassociate into a solution and anhydrous Na_2SO_4, this behavior is not unexpected. As the PCM is heated, the frozen solution reaches its melting point first, at a temperature close to 0°C. Upon further heating, the still frozen $Na_2SO_4{\cdot}10H_2O$ melts at the PCM's phase transition temperature of 33.2°C. Since a portion of the bulk PCM has disassociated (indicated by the peak near 0°C), the lower H_f value found is to be expected. These results are consistent with findings by Furbo, who stated that at temperatures below the phase transition temperature, an incongruently melting PCM will consist of three district layers [73]. From top to bottom, these layers are a saturated salt solution, a layer of crystalized PCM, and a sedimentary layer of anhydrous PCM.

As seen in Table **2**, it has been suggested that the melt temperature of $Na_2SO_4{\cdot}10H_2O$ can be reduced through the addition of H_2O. This concept was explored as the melt temperature of $Na_2SO_4{\cdot}10H_2O$ was slightly above than that required for the proposed cold storage system. In order to test the impact of additional water on both the melting temperature and heat of fusion of $Na_2SO_4{\cdot}10H_2O$, 25 wt% extra H_2O was added to this salt before it was tested by DSC. The initial DSC melting results for $Na_2SO_4{\cdot}10H_2O$ + 25% H_2O are presented in Figure **12** (the solid dark grey line). Although T_m for this mixture was found to be reduced slightly from the pure $Na_2SO_4{\cdot}10H_2O$ PCM (30.7 vs. 33.2°C), it was still well in excess of that suggested by the literature (24.0°C). H_f was also found to be reduced relative to $Na_2SO_4{\cdot}10H_2O$ without extra water (174.5 vs. 190.6 J/g).

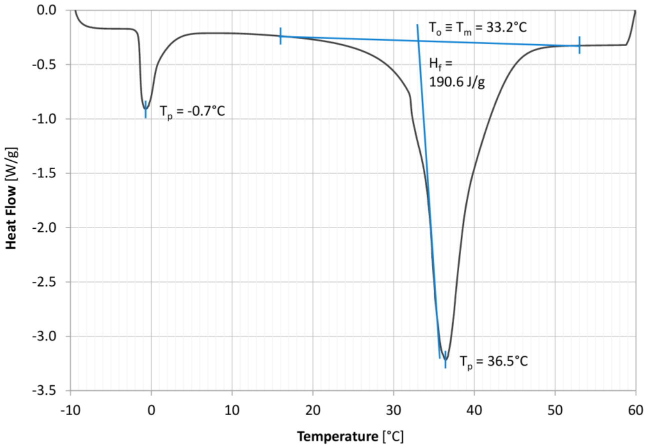

Figure 11: DSC Melting Curve of $Na_2SO_4{\cdot}10H_2O$.

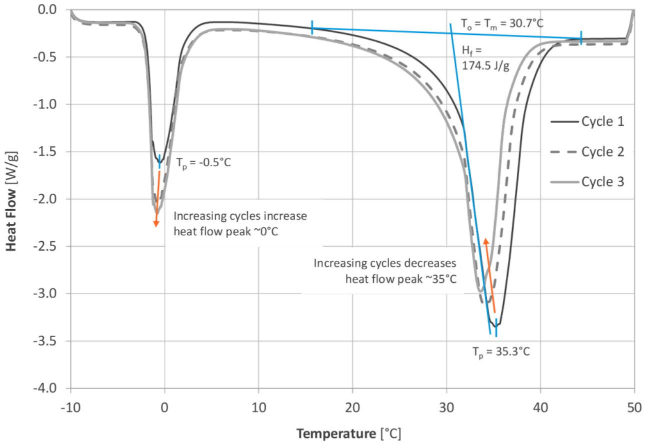

Figure 12: Change in DSC Melting Curve of $Na_2SO_4{\cdot}10H_2O$ + 25% H_2O with Cycling.

The DSC melting curves of Figure **12** show a similar trend to that for pure $Na_2SO_4 \cdot 10H_2O$ in Figure **11**, where a peak forms around 0°C and at the tetrahydrate's melting temperature. For the case with 25 wt% extra H_2O in Figure **12**, it can be seen that the peak at ~0°C is larger than that for $Na_2SO_4 \cdot 10H_2O$ without extra water (see Figure **11**). This indicates that the added extra water is preferentially entrained in the salt solution rather than forming a stable compound with the $Na_2SO_4 \cdot 10H_2O$.

In order to test the stability of $Na_2SO_4 \cdot 10H_2O$ + 25% H_2O with cycling, the DSC sample was subjected to three thermal cycles. Heat flow traces for the melting portions of these three cycles are seen in Figure **12**. These results qualitatively show that the peak at the tetrahydrate melt temperature (~35°C) decreases in height with increasing cycles, while the peak at ~0°C simultaneously increases in height. This behavior is a clear indication of phase separation within this salt brought about through thermal cycling. Given the large magnitude of this change in peak height with a very small number of cycles, it is suggested that $Na_2SO_4 \cdot 10H_2O$ + 25% H_2O is extremely unstable with cycling and measures must be taken to prevent this separation if this PCM is to have any commercial utility.

CONCLUSIONS

Differential scanning calorimetry (DSC) has been demonstrated as an effective technique for analyzing both the melt temperature (T_m) and latent heat of fusion (H_f) of low-temperature phase change materials. While DSC was found to be capable of measuring the thermal properties of a PCM during melting, it was found that supercooling prevents accurate DSC analysis during freezing. This limitation arises from both the small DSC sample size and relatively high cooling rate (7°C/min) of the DSC.

Two $CaCl_2 \cdot 6H_2O$-based eutectics were found, which have favorable thermal properties in the 20-30°C phase transition temperature range. The first, $CaCl_2 \cdot 6H_2O$ + KNO_3 was found to have a tunable melt temperature based on the quantity of KNO_3 added. PCM melt temperature was found to vary significantly as the weight percentage of KNO_3 was varied between 0% (28.3°C) and 10.8% (15.3°C). When a mixture of 7 wt% KNO_3 was selected for closer analysis, a T_m of 19.6°C and H_f of 120 J/g were found using DSC testing. A second eutectic mixture of $CaCl_2 \cdot 6H_2O$ + 18 wt% $MgCl_2 \cdot 6H_2O$ was found through experimentation and supported through phase diagram modeling. DSC testing of this eutectic found it to melt at 21.9°C with an H_f of 149 J/g.

DSC testing of Glauber's salt revealed significant phase separation for this material. Phase separation of this salt was evident by the appearance of two distinct phase transition heat flux peaks before any cycling was undertaken. One peak corresponds to the melt point of the $Na_2SO_4 \cdot 10H_2O$, while the other occurs at the melting point of a water/salt solution. When this PCM was cycled three times in the DSC, the peak corresponding to the $Na_2SO_4 \cdot 10H_2O$ melt temperature was found to decrease in size with a corresponding increase in size of the water/salt solution peak.

ACKNOWLEDGMENTS

The information, data, or work presented herein was funded in part by the Advanced Research Projects Agency – Energy (ARPA-E), U.S. Department of Energy.

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Received on 06-07-2019 Accepted on 19-11-2019 Published on 30-12-2019

DOI: http://dx.doi.org/10.15377/2409-5826.2019.06.8