



High Temperature Phase Change Materials for Thermal Energy Storage Applications

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HIGH TEMPERATURE PHASE CHANGE MATERIALS FOR THERMAL ENERGY STORAGE APPLICATIONS

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Abstract

To store thermal energy, sensible and latent heat storage materials are widely used. Latent heat thermal energy storage (TES) systems using phase change materials (PCM) are useful because of their ability to charge and discharge a large amount of heat from a small mass at constant temperature during a phase transformation. Because high-melting-point PCMs have large energy densities, their use can reduce energy storage equipment and containment costs by decreasing the size of the storage unit. Using cascaded PCMs, with equally spaced melting points and with high thermal properties, the TES is significantly enhanced. However, currently there is not enough information on the thermal properties of molten salt systems at high temperatures.

Molten salt PCM candidates for cascaded PCMs were evaluated for the temperatures near 320°C, 350°C, and 380°C. These temperatures were selected to fill the 300°C to 400°C operating range typical for parabolic trough systems, that is, as one might employ in three-PCM cascaded thermal storage. Such systems require a series of PCMs with melting points spanning the range of TES. The molten salt systems considered in this study were KNO₃-KCl-KBr, NaCl-KCl-LiCl and MgCl₂-KCl-NaCl. Because the majority of the salts studied were hygroscopic, a handling and mixing protocol under controlled atmosphere was employed. The mixing procedure was carefully controlled because the sample weight required for the thermal property tests is on the order of a few milligrams, so a perfectly homogenized sample is essential for accurate results. Heat capacity, latent heat, transformation temperatures, thermal stability, and viscosity were measured. Before performing these evaluations, chemical stability (corrosion) of the container materials with the molten salts was evaluated in a controlled atmosphere furnace under nitrogen gas. The materials tested were 316 stainless steel (SS316), high purity aluminum (Al1100), aluminum-manganese alloys (Al3003) and aluminum oxide (Al₂O₃). Based on the results, the best candidate for temperatures near 320°C was the molten salt KNO₃-4.5wt%KCl. For the 350°C and 380°C temperatures, the evaluated molten salts are not good candidates because of the corrosiveness and the high vapor pressure of the chlorides.

Keywords: phase change material (PCM), molten salts, melting point, latent heat, heat capacity, viscosity

1. Introduction

It is clearly understood that lower overall costs are a key factor to make renewable energy technologies competitive with traditional energy sources. Energy storage technology is one tool that can increase the value and reduce the cost of all renewable energy supplies.

Concentrating solar power (CSP) technologies have the ability to dispatch electrical output to match peak demand periods by employing thermal energy storage (TES). This attribute increases the value of the renewable energy and minimizes grid integration concerns. In addition, TES can reduce the levelized cost of energy (LCOE) if the levelized cost of the TES system is low compared to the additional revenue provided by greater utilization of the power block. In order to achieve these lower costs, energy storage technologies require efficient materials with high energy density.

More than 400 megawatts (MW) of CSP capacity are currently in place in the southwestern United States [1] and greater capacity is in place in Spain. There are plants under construction that would add more than 650 MW of capacity in Arizona and California. One of these plants with a capacity of 280 MW is based on the parabolic trough technology and thermal storage using molten salts—similar in design, but larger than the Andasol plants in Spain [2, 3].

The value of TES is in enabling CSP technologies to play an increasingly significant role in providing sustainable power generation [1]. CSP plants with TES can generate electricity when sunlight is not available, for example, during momentary cloud transients, which otherwise disrupt electricity generation and cause widely varying power output, and during evening hours when electricity is highly valued. TES also allows for more efficient use of the turbine and other power-block components. These features provide an economic incentive for the addition of TES. Without TES, CSP is an intermittent power resource that depends on sunlight availability.

Sensible and latent heat storage materials are widely used to store thermal energy. While sensible storage systems are simpler, latent heat TES systems using phase change materials (PCM) are useful because of their greater energy density. PCM technology relies on the energy absorption/liberation of the latent heat during a physical transformation. Unlike vapor-liquid transformations, solid-liquid transformations produce large enthalpy changes without substantial density changes. Because of this behavior, salts and metallic alloys are good candidates for PCMs. Ideally, these materials should have a specific melting point and high heat of fusion, and offer favorable characteristics such as high working temperatures (more than 500°C), low vapor pressure, good thermal and physical properties, low corrosivity and toxicity, and, of course, low cost.

Because high-melting-point PCMs have large energy densities, their use can reduce energy storage equipment and containment costs by decreasing the size of the storage unit. The optimum input and output temperature of the energy storage equipment is determined by the melting point of the PCM, while the heat capacity of the TES system is determined by the PCM latent and sensible heats.

The knowledge of the thermal properties of a particular PCM is important for its selection as a thermal storage material. To decrease the LCOE, CSP technologies rely on different simulations to increase the thermal energy storage capability. Using cascaded PCMs, with equally spaced melting points and with high thermal properties, the TES is significantly enhanced [7]. However, currently there is not enough information on the thermal properties of molten salt systems at high temperatures.

2. Goals and Objectives

The goal of this work is to create a PCM database for TES applications, in particular, to enable solar parabolic trough plants to operate with greater efficiency and lower electricity costs.

The focus of the research was the characterization of the thermal and chemical properties of candidate materials for latent heat TES. Candidate PCMs were identified in a temperature range from 300°C to 500°C, with initial emphasis given to materials with melting points near 320°C, 350°C, and 380°C. These temperatures were selected to allow for a three-temperature, cascaded PCM storage system for current parabolic trough power plants. The physical properties most relevant for PCM use were reviewed from the candidate selection list. Specific objectives for this work were: 1) preparation of homogeneous molten salt PCM formulations minimizing water absorption and contamination; 2) chemical stability evaluations of the PCMs with some container materials, like stainless steel 316 (SS316), aluminum alloys (Al1100 and Al3003), and aluminum oxide (Al_2O_3); and, 3) thermal properties characterization of the PCMs, including identifying phase change transformation temperatures with their associated latent heats, solid and liquid heat capacities, and viscosities.

3. Background

Accurate knowledge of the heat of fusion, melting point, thermal conductivity, heat capacity of the two phases, and corrosivity of the PCM are essential for the design of TES systems employing phase change. The phase transformation should occur at only one invariant temperature to maximize the efficiency of the PCM when absorbing and storing the heat. For parabolic trough applications, the temperature range of interest for the PCMs is from 300°C to 500°C. In 2007, Michels and Pitz-Paal proposed a cascaded PCM system using a series of five PCMs spanning the operating range from approximately 300°C to 400°C. Such a design was estimated to have advantages over the two-tank sensible TES system, but was complex. Reducing the number of temperature steps could reduce system complexity. This work seeks to identify candidate materials with melting point temperatures near 320°C, 350°C, and 380°C [7].

Thermal properties of salt blends are highly sensitive to composition and large discrepancies have been found amongst the literature regarding the melting points and thermal properties associated to a particular chemical composition for molten salt systems. The identification of an accurate melting point of a PCM formulation as well as its thermal properties is key for advancing TES technologies. The candidate PCM identification was obtained using phase diagrams in which the eutectic reactions occur in the temperature range evaluated. A eutectic reaction occurs at an invariant and constant temperature in which a liquid phase transforms into different solid phases during cooling. The eutectic temperature represents the minimum temperature at which the liquid phase is stable in that particular system. The eutectic composition melts at only one constant temperature, which is a valuable feature for a cascaded PCM.

4. Approach

The identification of candidate PCMs was performed by a thermochemical evaluation using different sources: Phase Diagrams for Ceramists [4], the NIST Phase Diagrams Database [5], FactSage thermochemistry software [6], and the open literature [7-11]. Discrepancies were found not only with the chemical compositions but also with the eutectic and other invariant reaction temperatures.

The lack of information regarding the molten salts at high temperatures, as well as the discrepancies in the invariant temperatures and compositions, has made the characterization of candidate molten salts of interest. The characterization was performed following strict protocols for handling unstable samples to obtain perfectly mixed and dried samples. Molten salt candidates for cascaded PCMs were evaluated for temperatures between 308°C and 380°C. The molten salt systems considered in this study are shown in Table 1.

Because the majority of the salts studied were hygroscopic, a handling protocol under controlled atmosphere was employed. The individual salts, acquired from Alfa-Aesar and Sigma Aldrich with purity levels greater than 99%, were placed in a muffle furnace at 120°C for at least 24 hours. Once dried, they were placed inside a dry box under nitrogen gas to be weighted in a balance with a resolution of 0.0001g, and combined at a specific ratio. To mix them, they were placed in a ceramic container. This jar was sealed inside the dry box to avoid exposure to air during the 30-minute mixing process that was performed in a powder mixer. The mixing procedure was carefully controlled because the sample weight required for the thermal property tests is on the order of a few milligrams, and a perfectly homogenized sample is essential for accurate results.

Heat capacities, latent heats, transformation temperatures and thermal stability of the PCMs were evaluated using a Mettler-Toledo Differential Scanning Calorimeter (DSC) and Thermogravimetric Analyzer with DSC (TGA/DSC). Viscosity measurements were obtained using a TA Instruments Rheometer AR2000ex. Before performing these evaluations, chemical stability (corrosion) of the DSC and TGA/DSC container materials with the molten salts was evaluated in a controlled atmosphere furnace under nitrogen gas at 450°C over two hours. The materials tested were 316 stainless steel (SS316), high purity aluminum (Al1100), aluminum-manganese alloys (Al3003) and aluminum oxide (Al₂O₃). The selected time of two hours corresponds with the longest exposure time of the crucibles with the molten salts during the DSC and TGA/DSC tests.

Sample	Molten Salt System, wt.%	Reported values		Source
		T _m , °C	ΔH _m , J/g	
6A1	92.81KNO ₃ -7.18KCl	308	-	[4]
6A2	97KNO ₃ -3KCl	~315	-	[4]
6A3	95.5KNO ₃ -4.5KCl	320	74	[7]
6B	90.72KNO ₃ -9.28KBr	328	-	[4]
6C1	89.98KNO ₃ -2.95KCl-7.06KBr	320	-	[4]
6C2	80.69KNO ₃ -7.44KCl-11.87KBr	342	140	[8]
1A	7.87NaCl-50.88KCl-41.25LiCl	344	-	[4]
1B	34.81NaCl-32.29KCl-32.90LiCl	346	281	[8]
1C	9.491NaCl-48.43KCl-42.08LiCl	350	-	[4]
3B	60.00MgCl ₂ -20.4KCl-19.60NaCl	380	400	[7]

Table 1: Melting points (T_m) and heats of fusion (ΔH_m) of the molten salt PCMs systems. Values are those reported by the open literature.

Once the chemical stability of the container materials with the molten salts was established, the DSC and TGA evaluations were performed. To do this evaluation, the samples were placed and sealed in the DSC crucibles inside the dry box. The sealed crucibles were then tested in the DSC instrument. Some formulations were stable only in alumina, which cannot be sealed airtight. For such formulations, the TGA was initially performed to evaluate mass losses during heating caused by the vapor pressure of the molten salt components. After the thermal stability evaluation in the TGA, DSC was performed using the alumina crucibles. Because the rheometer is made of stainless steel, only the compositions that were found to be compatible with stainless steel could be run on the rheometer.

5. Results and Analysis

The corrosion test made it clear that all the crucible materials were stable in the nitrate formulations because they did not show any chemical attack from the KNO₃-KBr-KCl molten salt. Prior work with pure nitrates had established their compatibility with the same container materials. The chlorides severely dissolved aluminum metal (Al1100), and attacked the metal alloys to some degree but did not react with Al₂O₃. The NaCl-KCl-LiCl system, samples 1A and 1B, attacked stainless steel (SS316) and incurred mass losses of 0.54% and 1.38%, respectively. The system did not attack Al₂O₃ and the Al-Mn alloy (Al3003) during the testing period. MgCl₂-NaCl-KCl reacted in a small degree with Al3003 (mass loss of 0.02%) but severely attacked SS316 (mass losses of 1.90%).

DSC tests for the nitrates were performed using the aluminum (Al1100) crucibles to maximize the heat conduction between the sample and the DSC sensor. This way, the measured latent heat was more accurate. Three heating and cooling cycles were performed per sample. At least three samples of each nitrate's formulation were tested. The averages of the results are shown in Table 2.

As predicted by the FactSage software and the Phase Diagrams database, samples 6C1 and 6C2, from the ternary mixture KNO₃-KCl-KBr, are not eutectics. This system does not have a ternary eutectic. In fact, the composition 6C2 relies on a stability region for two phases under equilibrium: liquid and solid. The melting process for these compositions occurs inside a range of temperatures instead of at a fixed temperature, which is the case for eutectic points. This temperature range occurs between the solidus boundary (T_{mi}: beginning of melting during heating, or T_{sf}: end of solidification during cooling) and the liquidus boundary (T_{mf}: end of melting during heating, or T_{si}: beginning of solidification during cooling). These samples showed a melting temperature span of about 36°C and 77°C, respectively.

Sample	Heating				Cooling				SC, °C
	T _{mi} , °C	T _{mf} , °C	ΔT _m , °C	ΔH _m , J/g	T _{si} , °C	T _{sf} , °C	ΔT _s , °C	ΔH _s , J/g	
6A1	321.18	333.15	11.97	70.75	327.43	321.78	5.65	70.48	5.72
6A2	320.67	-	-	87.62	324.40	321.92	2.48	88.04	3.73
6A3	319.68	-	-	82.05	320.20	-	-	83.66	0
6B	335.08	372.05	36.98	81.87	367.13	336.54	30.59	82.87	4.92
6C1	327.73	363.45	35.72	75.29	359.35	329.34	30.01	76.93	4.10
6C2	326.58	403.74	77.16	75.89	404.37	324.41	79.96	77.30	0

Table 2: Melting and solidification thermal properties of KNO₃-KCl-KBr system. (T_{mi}, T_{mf}: initial and final melting temperatures; T_{si}, T_{sf}: initial and final solidification temperatures; ΔT_m, ΔT_s: melting and solidification temperature range; ΔH_m, ΔH_s: heats of melting and solidification; SC: supercooling)

The predicted eutectic points for composition 6A1, KNO₃-KCl at 308°C and composition 6B, KNO₃-KBr at 328°C were not obtained. These formulations melted in a temperature range of about 12°C and 37°C, respectively.

For all the KNO₃-KCl samples, the beginning of melting occurred on average at 320°C. The approach to find the eutectic composition was to change the chemical composition by adding small amounts of KCl and then evaluating the melting temperature range. Those samples in which only one temperature is resolved in DSC are the ones closest to the eutectic composition. The DSC peak for these formulations should be sharp with no bumps and no changes in the slopes, which represent changes in the phase transformation.

Formulations 6A2 and 6A3 were prepared and characterized using 95.5wt%KNO₃-4.5wt%KCl (6A3) as the possible eutectic composition with 320°C as the invariant eutectic point, with no supercooling behavior. This sample produced the sharpest melting and solidification peaks with an average heat of fusion/solidification of about 82.86 J/g. This value is higher than the reported heat of fusion of 74 J/g [7]. This discrepancy could be related to the purity level of the single components and the NREL's strict protocols followed for mixing and handling of the molten salts that produced homogenous, contamination-free, and moisture-free materials. Because of the presence of KCl in this formulation it is recommended that a long-term corrosion test with container materials be performed to corroborate the use of KCl as one of the PCM candidates for the cascaded thermal storage system.

Previous evaluations in the DSC using KNO₃ reported a melting point of 335.32°C with a heat of fusion of 97.25 J/g. Adding small amounts of KCl (3wt.% and 4.5wt%) to KNO₃ decreased the heat of fusion of pure KNO₃ to 87.62 J/g and 82.05 J/g, respectively. This decrease of 10% to 16% is substantial for such small quantities of chloride additions. KNO₃ is a viable candidate for PCM but has a higher melting point.

The formulations with only chloride anions were thermally and chemically unstable. Mass losses occurred during the tests caused by the vaporization of the salts. These samples were extremely difficult to handle and characterize. One of the big inconveniences was the presence of adsorbed water that can react with the salt, generating hydrochloric gas during water removal at high temperatures. TGA/DSC and DSC results for these samples for three heating and cooling cycles are shown in Table 3. There were mass losses while performing the heating cycles for each sample. The associated heat of fusion obtained from the TGA/DSC analysis was normalized to the real mass value obtained from the test. Even after adjusting the latent heats there was a decrease of these values among cycles, which meant that the samples are thermally unstable. The NaCl-KCl-LiCl system was also tested in the DSC because it was less aggressive and more stable than MgCl₂-KCl-NaCl.

The melting point of the sample 3B (60.00wt%MgCl₂-20.4 wt%KCl-19.60wt%NaCl) was an average 387.60°C, which is around 8 degrees higher than the value reported by the literature (380°C). The

solidification occurred with 10.90°C of supercooling to 376.60°C. The sample's heat of fusion was roughly 199 J/g, which is only 50% of the reported value (400 J/g) and 68% of the calculated value from FactSage (290 J/g). The measured values using the TGA were not as accurate as the values obtained in the DSC. The latter has 120 thermocouples to control and measure the temperatures that are related to the heat flow measurement. This feature makes this instrument more accurate than the TGA, which has only one thermocouple.

DSC results from the NaCl-KCl-LiCl system (Table 3) showed the decreasing behaviour of the latent heat, which is related to the mass losses amongst heating cycles. The melting point of the sample 1B (34.81 wt%NaCl-32.29 wt%KCl-32.90wt%LiCl) was on average 352.89°C, while the value reported in literature is 346°C. Solidification occurred with 2.18°C of supercooling to 350.70°C. The heat of fusion of this sample was around 138 J/g which is only 49% of the reported value (281 J/g). This measured value is closer to the one predicted by FactSage for this composition, which was 146 J/g. This formulation is good for a 350°C melting point PCM, but considerations must be made for its vaporization and thermal instability. Al3003 seems to be resistant to this chloride system during the testing period (two hours), but long-term corrosion tests must be performed with this alloy to evaluate its real chemical stability in the presence of this PCM.

The discrepancies in the latent heats are most likely related to the fact that these chlorides are thermally and chemically unstable and are hygroscopic materials. The MgCl₂-KCl-NaCl system, with a melting point of 387.60°C, is probably too high for use in current parabolic trough plants operating with biphenyl/diphenyl oxide synthetic-oil heat transfer fluids. Additionally, this chloride system is extremely unstable and chemically aggressive.

Sample-cycle	Heating		Cooling		SC, °C	Analyzer
	T _m , °C	ΔH _m , J/g	T _s , °C	ΔH _s , J/g		
1B-1	359.63	144.93	350.88	135.22	-	DSC
1B-2	353.40	142.99	350.35	119.92	3.05	DSC
1B-3	352.37	127.33	350.88	114.25	1.49	DSC
1B-Average	352.89	-	350.70	-	2.18	DSC
1B-1	360.42	164.18	347.33	124.05	13.09	TGA/DSC
1B-2	356.73	138.55	347.39	124.35	9.34	TGA/DSC
1B-3	356.26	125.37	347.33	122.73	8.93	TGA/DSC
1B-Average	356.50	-	347.35	-	9.14	TGA/DSC
3B-1	393.90	197.92	376.30	198.30	17.60	TGA/DSC
3B-2	387.80	199.50	376.27	195.91	11.53	TGA/DSC
3B-3	387.39	197.59	377.13	183.74	10.26	TGA/DSC
3B-Average	387.60	-	376.60	-	10.90	TGA/DSC

Table 3: Melting and solidification of 34.81wt.%NaCl-32.28wt.%KCl-32.91wt.%LiCl (1B) and 60.00wt%MgCl₂-20.4 wt%KCl-19.60wt%NaCl (3B) using DSC and TGA/DSC. Due to mass losses during cycles, the latent heats of melting and solidification (ΔH_m, ΔH_s) were adjusted. (T_m, T_s: melting and solidification temperatures; SC: supercooling).

Heat capacity (Cp) was measured only for the KNO₃-KCl-KBr system because these PCMs are thermally and chemically stable under the test conditions. The Cp was measured following the standard ASTM E1269-5. Three heating and cooling cycles were performed per sample. The average of the solid and liquid heat capacities per each PCM are shown in Figure 1. For all the samples, the solid heat capacity increased proportionally with temperature, and the liquid heat capacity had a constant behavior up to 500°C. The candidate PCM KNO₃-4.5wt%KCl has high solid and liquid heat capacities compared with the other PCMs evaluated in the KNO₃-KCl-KBr system. The heat capacities of pure KNO₃ were 1.42 J/g.K at 350°C for the

solid and 1.47 J/g.K for the liquid. Adding 4.5wt%KCl to KNO₃ decreased the liquid heat capacity to about 1.31 J/g.K. This decrease of 11% substantially affects the energy density of this candidate PCM when compared with pure KNO₃.

The viscosity of the samples KNO₃-3wt%KCl and KNO₃-4.5wt%KCl was evaluated at 335°C. The average values were 3.19 cP and 3.23 cP, respectively. These values are 18% to 20% higher than the viscosity of KNO₃ which is about 2.7 cP at 350°C. The viscosities of the evaluated PCMs are approximately threefold higher than the viscosity of the synthetic oil (Therminol VP-1®) used for parabolic trough heat transfer fluid. However, these candidate PCMs have an acceptable viscosity because they are not required to flow in the storage system.

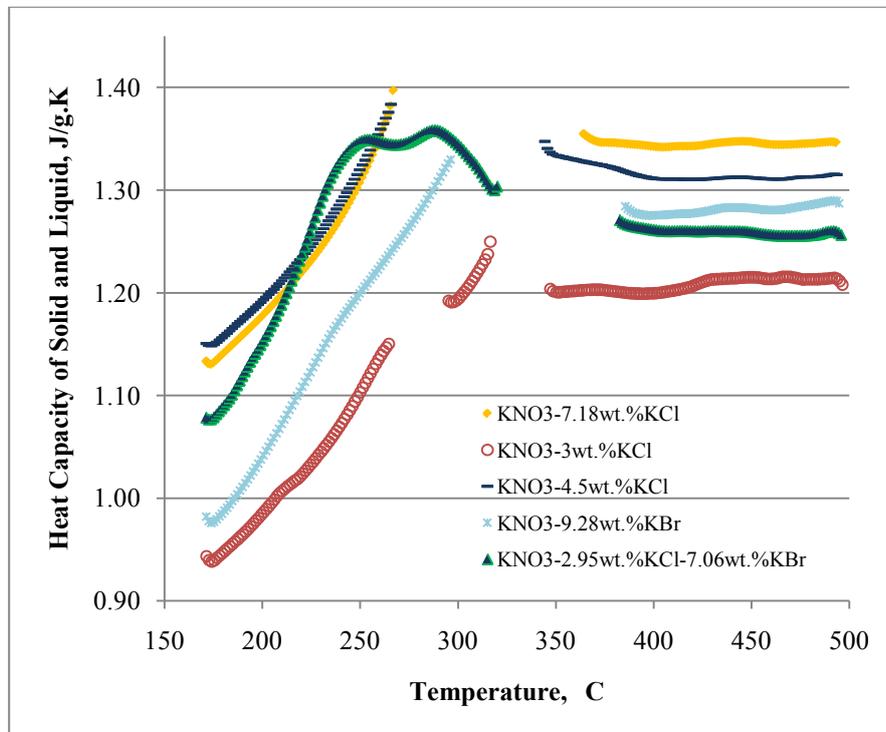


Figure 1: Averaged heat capacity of solid and liquid phases for KNO₃-KCl-KBr system. The solid heat capacities are the lines with a positive slope while the liquid heat capacities are the constant values. Heat capacity spikes to infinity during phase change around 320°C.

6. Conclusions and Recommendations

Based on the results, the best molten salt candidate for a 320°C PCM was the KNO₃-4.5wt%KCl formulation. This salt had a defined eutectic behavior with no supercooling. The melting/solidification process occurred at ~320°C with a latent heat of ±82.86 J/g. The heat capacities were relatively high: solid heat capacity was 1.40 J/g.K at 270°C and liquid heat capacity was 1.31 J/g.K at greater than 380°C. The viscosity was 3.23 cP which is relatively good for a PCM candidate. However, comparing this formulation with the sensible heat solar salts currently employed in indirect two-tank TES systems for the parabolic trough, the thermal properties are relatively poor. The values should be greater than 100 J/g for latent heat and greater than 1.50 J/g.K for heat capacity. When comparing the thermal properties of KNO₃-4.5wt%KCl with those of pure KNO₃ (melting point of 335°C), the reduction in the heat of fusion and the liquid heat capacity decreases the energy density of the KNO₃ when adding small amounts of KCl.

The molten salts evaluated for the target melting point temperatures of 350°C and 380°C are not good candidates because of the corrosiveness and the high vapor pressure of the chlorides. For these temperatures other candidates must be considered. NREL is currently evaluating non chloride salt blends with melting

points between 380°C and 390°C. Finding a salt with a melting point of the intermediate temperature of 350°C has been extremely difficult. All the possible candidates are mixtures of chlorides and fluorides, which are corrosive.

Future evaluations should consider long-term chemical stability (corrosion) of the construction materials in the molten salts as well as thermal conductivity and density measurements. In this way, the effectiveness of the thermal storage could be evaluated based on the energy density of the candidate PCM.

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