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The Use of Sodium Chloride & Aluminum as Phase Change Materials for High Temperature Thermal Energy Storage Characterized by Calorimetry

by

Laura Solomon

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Date

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Mechanical Engineering and Mechanics

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ABSTRACT

Encapsulated phase change materials (EPCM) have a great deal of potential for the storage of thermal energy in a wide range of applications. The present work is aimed at developing encapsulated phase change materials capable of storing thermal energy at temperatures above 700°C for use in concentrated solar power (CSP) systems. EPCM with a phase change material (PCM) with both a salt (sodium chloride) and a metal (aluminum) are considered here. Sodium chloride and aluminum are effective storage mediums because of their high melting points and large latent heats of fusion, 800°C and 660°C and 430kJ/kg and 397kJ/kg, respectively. Based on the heat capacities and the latent heat of fusion, for a 100 degree temperature range centered on the melting point of the PCM, 80% of the energy stored by the sodium chloride PCM can be attributed to the latent heat and 79% for the aluminum PCM. These large fractions attributed to latent heat have the potential for making EPCM based thermal energy storage devices smaller and less expensive. To study the performance of the candidate PCMs considered here, a specialized immersion calorimeter was designed, calibrated, and used to evaluate the storage capabilities of sodium chloride and aluminum based EPCMs. Additionally, the EPCMs were studied to ensure no loss of capacity would occur over the lifetime of the EPCM. While no reduction in the storage capacity of the sodium chloride EPCMs was found after repeated thermal cycles, there was a decrease in the storage capacity of the aluminum EPCMs after prolonged exposure to high temperatures.

CHAPTER 1

INTRODUCTION

1.1 Motivation

Before the development of coal as a fuel source during the mid-19th century, all energy was a form of renewable energy, whether it was water powering a mill, the burning of wood, or just simple human labor. The use of coal and other fossil fuels, however, rendered the previous sources of energy inefficient and powered the industrial revolution. For over a hundred years the cost and abundance of fossil fuels made renewable energies monetarily impractical. However, events of the past several decades have solidified the realization that the earth's resources are finite and that they are rapidly being depleted. This understanding has intensified research into finding and developing a suitable, cost-competitive renewable energy source as a replacement.

One of the many technologies being developed as a renewable replacement for fossil fuels is that of solar energy. While the idea of harnessing the sun's power is not a new one, a way to make solar energy as efficient as current fossil fuel processes needs further development. The gap between fossil fuel power plants and solar power plants is clearly shown by breaking down energy usage in the United States in 2011. The total energy usage by the United States in 2011 was 97.5 quadrillion Btu. Only 9% of the total energy usage was from renewable sources. The two main sources of renewable energy were biomass (48%) and hydro-electric power (35%), while the other 17% consisted of geothermal (2.5 %), wind (13%), and solar, which contributed only 1.5% [1].

Solar energy was the smallest contributor to renewable energy because of the low capacity factor of solar power plants. The capacity factor of a power plant is a measure of what percentage of a plant’s potential output is actually output over a certain period of time. For example, a conventional coal-fired power plant can have a capacity factor of 85%. In contrast, a solar power plant only has a capacity factor of about 18% [2]. The low capacity factor of solar power plants can be attributed to the limited hours of solar radiation. There are only an approximate total of 3,000 hours of daylight in a year, which is only 34% of a year’s length. This total is further decreased when inclement weather is taken into consideration. These effects highlight that, like most renewable energies, solar energy is intermittent. Therefore, for solar technology to become as efficient as current fossil fuel technology, it must be able to overcome these transients.

There are two different approaches that current solar technology can be divided into; using photovoltaic cells to directly convert solar irradiation into electrical energy or using concentrated solar power (CSP) systems that convert solar energy into thermal energy which is then used to generate electricity. Both of these approaches have to overcome the intermittencies inherent to solar power. To overcome these transients it is necessary to utilize a form of energy storage to ensure that the energy production is not disrupted. Of the many approaches to storing energy, when it comes to storing solar energy the use of thermal energy storage (TES) is economically promising as well as thermodynamically attractive. The use of TES would also alleviate any drop in power output from a solar power plant during intermittent periods of solar irradiation by storing solar energy in a medium during times of peak solar irradiation and then releasing the stored energy during times of low solar irradiation.

1.2 Thermal Energy Storage

Thermal energy storage occurs when heat is either added or removed from a storage medium. Examples of TES are found everywhere. Hot water that is used for household heating is a form of TES, as are ice used for cooling, hot and cold packs, and the hot rocks used in saunas. In all of these examples, the object undergoes a temperature change, which causes a change in the enthalpy of the medium. This change in enthalpy corresponds to the amount of thermal energy that has been stored or removed from the medium. TES is divided into three major classifications; sensible heat storage, latent heat storage, and chemical storage.

The most common form of TES is that of sensible heat storage. Sensible heat storage takes advantage of the mass of the material, the temperature difference that the material is exposed to, and the appropriate heat capacity of the material depending on the state of the material. With sensible heat storage, there is no phase change in the material during the energy storage process. Some common materials that are used for sensible heat storage include rocks, bricks, water, and oils. An example of sensible heat storage is that of a hot water bottle. Energy is stored in the water when the water bottle is heated and that stored energy can be slowly released over time for use in alleviating muscle pains. However, a drawback of using sensible heat storage alone as the method of TES is the large volume of material needed ($10^6 m^3$) to store and release the required amounts of energy over the large time intervals experienced at CSP plants, in the order of 100MWe for over six hours [3] [4].

To decrease the volume of material required when using sensible heat storage alone, one could utilize the latent heat of phase change. Unlike sensible heat storage, which requires a temperature difference, latent heat storage occurs at a constant temperature while the material is undergoing a phase change. Ice melting in a drink is a simple example of the usage of latent heat storage. The amount of water placed in a drink in the form of ice is less than the amount of liquid water that would be required to achieve the same change in drink temperature. This exemplifies how with a thoughtful choice of material, taking into consideration its melting temperature, a greater amount of thermal storage can take place per unit mass by utilizing latent heat storage along with sensible heat within a temperature range bracketing the materials melting point than with the use of sensible heat storage alone.

Latent heat storage occurs any time a material experiences a phase change. Phase changes occur predominately in two different ways; a solid-liquid transition or a liquid-gas transition. In a liquid-gas transformation, also known as vaporization, the phase change enthalpy is large. This high latent heat of vaporization allows for large amounts of energy storage. However, due to the large volume expansion of the medium experienced during vaporization, it would require either a large storage tank to minimize the increases in pressure or a fixed volume container strong enough to withstand the pressure increase without rupturing. Both of these situations make the use of a liquid-gas transition impractical for a closed system. Additionally loses to the environment that can occur in an open system making using a liquid gas transition a poor choice for TES.

By contrast the volumetric expansion that occurs during a solid to liquid transformation, or melting, is only about 10%, far less than the expansion that occurs during vaporization. The smaller increase in volume corresponds to a smaller increase in pressure within a closed system as well. Although the latent heat of fusion is typically lower than the latent heat of vaporization, the smaller increase in volume and pressure makes a solid-liquid transition more favorable. A system designed to accommodate the expansion and pressure increase that occurs during the phase change could then be utilized to increase the amount of thermal energy stored in a material on a per unit mass basis over a system using only sensible heat storage.

The third and final form of TES is that of chemical energy storage, which stores and releases energy through endothermic and exothermic reactions. Due to its high-energy storage density and controllability, chemical energy storage is a highly attractive method for TES. However, due to a lack of certainty in physio-chemical and thermodynamic properties, the use of chemical storage is highly limited [5][6].

With all of the advantages offered by the utilization of latent heat storage as a form of TES, it has become a rapidly growing field of research and development. In particular, research into the use of phase change materials (PCMs) that undergo a solid-liquid transition at ever-increasing temperatures has become a topic of great interest.

1.3 Phase Change Materials

There are generally two types of PCMs; organic and inorganic. Organic PCMs include paraffin and fatty acids while inorganic PCMs include salts, salt hydrates, salt eutectics, and metals. Current research has focused on the numerous PCMs that can be used at low temperatures, those around 120°C [7]- [13]. More recently, research into PCMs with melting points above 300°C has been conducted using sodium nitrate, a sodium chloride-magnesium chloride eutectic with promising results [14]. While these existing PCMs have numerous applications, there is a need for PCMs with melting points above 600°C for use in the temperature range required for CSP applications where electricity is generated from solar power using gas turbines operating on a Brayton cycle. Recent research was performed using magnesium chloride as a PCM at temperatures up to 750°C with good results for use in TES [15].

Some early approaches into TES for CSP application have used tanks of high temperature PCMs with internal tubes used to transfer the energy between the solar collectors, storage medium, and turbine (Horst Michels in 2007) [14]. The difficulties with these large systems were obtaining good heat transfer between the heat transfer fluid and the PCM, particularly during the discharge process due to the low thermal conductivity of current PCMs. A potential solution to this problem is to encapsulate small amounts of the PCM into a shell and to use numerous capsules rather than using one large container of the PCM. This would increase the area of the heat transfer surfaces, which in turn decreases the total heat transfer time [16].

However, this leads to the dilemma of what geometry and thickness of a capsule is required. The geometry and thickness of the capsule are important because the capsule needs to be able to allow room for the volumetric expansion of the PCM while also maximizing the heat transfer surface area and withstanding the stress caused by the increase in internal pressure [17] [18]. Additionally, care needs to be taken to ensure that the PCM and capsule material are compatible. If the PCM and capsule are not compatible, corrosion or alloying between the two materials can occur, resulting in a decrease in the amount of thermal energy stored in the encapsulated phase change material (EPCM) over time.

The use of EPCMs to store solar energy at high temperatures, above 700°C, is a novel TES technology and would allow for TES usage at solar power plants that use Brayton cycle gas turbines. However, in order to continue to develop this technology, the thermo-physical properties of different PCMs need to be studied.

1.4 Current Objectives

The objective of the work presented here was to examine the performance of two high temperature candidate PCMs; one salt, sodium chloride (NaCl), and one metal, aluminum (Al), and to add to the development of EPCMs used for thermal storage in CSP systems at temperatures between 720°C and 850°C. In order to examine the performance of each candidate PCM, an immersion calorimeter was designed, calibrated, and used to conduct all calorimetry measurements. The calorimetry system was used to calculate the enthalpy stored in the two high temperature candidate PCMs, NaCl and Al, in order to judge their performance over time.

The design and calibration of the calorimetry system that was used is described in chapter 2. The calorimetry system was designed that when the sample EPCM samples were dropped in the system it would induce a large enough temperature change in the system that the enthalpy stored in each sample EPCM could be measured accurately. Chapters 3 and 4 detail the testing of the NaCl-stainless steel and Al-stainless steel EPCMs, respectively. After consideration of different geometries and materials it was determined that the best capsule design was that of cylindrical stainless steel capsules. The capsules are 2.54cm in diameter and 5.08cm in height and were filled with selected amounts of PCM such as to allow for the volumetric expansion that occurs during melting [19] [20]. Each sample was tested in the calorimetry system multiple times to determine the amount of thermal energy stored during each cycle and to determine if a loss of storage capacity occurred in the EPCM after multiple thermal cycles. A decrease in storage capacity would suggest that the PCM and capsule material are incompatible and do not make for a viable EPCM combination. Finally, Chapter 5 summarizes the findings of chapters 2-4 as to the overall performance of the calorimetry system and the two candidate PCMs.

CHAPTER 2

CALORIMETRY SYSTEM

In order to utilize TES at higher temperatures, further research into candidate PCMs with higher melting points is needed. Currently, there are three ways to study the properties of candidate PCMs; conventional calorimetry, differential scanning calorimetry (DSC), and differential thermal analysis (DTA). Both DCS and DTA can be quite accurate; however difficulties can arise because of the small sample sizes (1-10mg) used for testing. With such a small sample size, the properties determined by DCS or DTA may not represent the bulk properties of the material, especially for a hygroscopic substance such as NaCl. In order to avoid these difficulties, a specialized immersion calorimeter was designed, calibrated, and used for all testing needed of the two candidate PCMs [14].

2.1 Calorimeter System Design

The main component in the calorimetry system that was designed is silicone oil. The silicone oil was contained within a thin metal vessel that is 24cm in height and 21cm in diameter. The metal vessel was insulated to reduce the heat loss from the system to the surroundings by using 4mm foam. The original system design used two concentric cardboard guard cylinders to further isolate the system from the laboratory to reduce noise occurring in the measurements [14] [21] [22]. However, in order to further decrease the heat loss, the two cardboard cylinders were replaced with a concentric cardboard guard cylinder and two guard boxes each made of 5mm thick foam board, as depicted in Figure 1. The interior guard box is 30cm high by 28cm wide and the exterior guard box is 36cm high by 36cm wide. Each guard box was fitted with a lid to eliminate heat loss from the top of the system.

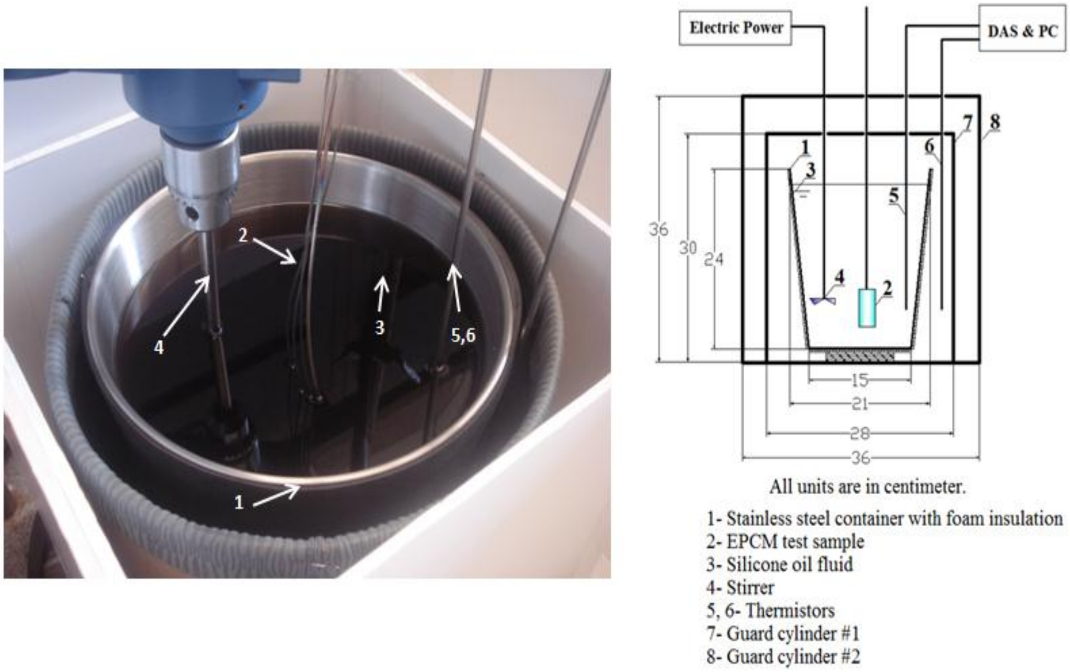

Figure 1. Calorimeter System Schematic and Photograph

The calorimeter system was designed in such a way that when the hot EPCM sample is immersed it induces a suitable temperature change within the calorimeter so an accurate calculation of the enthalpy change of the system can be made. If the temperature increase is too small the temperature measurements will not be as accurate, but if the change is too large problems can arise such as the generation of bubbles that can cause inaccuracies. Therefore the amount of silicone oil required was determined to be approximately 4.5kg [14][22]. The silicone oil that was chosen for use was Dynalene 600. It was chosen because of its relatively high flash point

(315°C), good thermal conductivity (0.156W/m K), and low vapor pressure (333 Pa). The low vapor pressure inhibits nucleation, the formation of bubbles, within the silicone oil when the hot EPCM sample is submerged, which would result in energy losses, and the good thermal conductivity provides a uniform temperature within the oil, ensuring that the temperature readings are accurate.

An electric mixer was used to further ensure a uniform temperature within the silicone oil during all experiments. The temperature of the silicone oil, which was considered to be the temperature of the calorimeter, was measured using a thermistor. Additionally the temperature of the air between the metal vessel and the guard cylinder was recorded in order to calculate the heat that was lost from the system during each experiment. The amount of heat lost from the system varied from experiment to experiment depending on the initial room temperature and the temperature of the sample.

In order to suspend the EPCM sample in the calorimeter to avoid heat loss through conduction to the container, a wire rod was welded to the top of each sample. After a thorough analysis of different materials and geometries, it was concluded that cylindrical stainless steel 304L shells would be used to encapsulate the NaCl and Al PCMs [19] [20]. Each capsule had a diameter of 2.54cm and a height of 5.08cm and was filled with a pre-selected amount of the PCM in order to leave a sufficient void volume, typically 20-30%, to accommodate the volume change experienced by the PCM during phase change. Each sample was then sealed with welded end caps. [17]

While the size of these capsules is relatively small, simulations have shown that the heat transfer process inside the sample is not an issue for the larger capsule size that would be used for TES at a CSP power plant [19] [20]. These simulations verify that results determined from the calorimetry experiments will represent the actual performance of EPCMs used as for high temperature TES.

2.2 Experimental Procedure

Before each experiment the mass of the silicone oil in the system was measured because of the slight decrease that occurred between experiments due to the removal of the EPCM samples at the end of each experiment. Additionally each EPCM sample was weighed to ensure that none of the PCM was leaking out of the samples. During the experiments each EPCM sample would first be heated in an electric furnace to a preselected temperature at least 50°C above the PCM's melting temperature; 850°C for NaCl and 720°C for Al.

Figure 2. The EPCM in a carbon steel cylinder during heating

The EPCM sample was then held at that temperature for over an hour to ensure a uniform temperature distribution within the sample and that all of the PCM had undergone a full phase change. In order to achieve uniform heating the sample was placed within a carbon steel cylinder during heating, see Figure 2. The temperature of the sample was measured during the heating process by securing three thermocouples around the sample using copper wire, as seen in Figure 3.

Figure 3. Three thermocouples secured around sample using copper wire

After being held at the desired charging temperature for over an hour, the hot EPCM was removed from the furnace and rapidly submerged into the calorimeter. The lids were then placed on the guard cylinders and additional pieces of foam board were used to cover any gaps between the lids. The temperature of the calorimeter and the air temperature inside the system were recorded as the EPCM and calorimeter reached an equilibrium temperature. However, the temperature of the EPCM sample was not

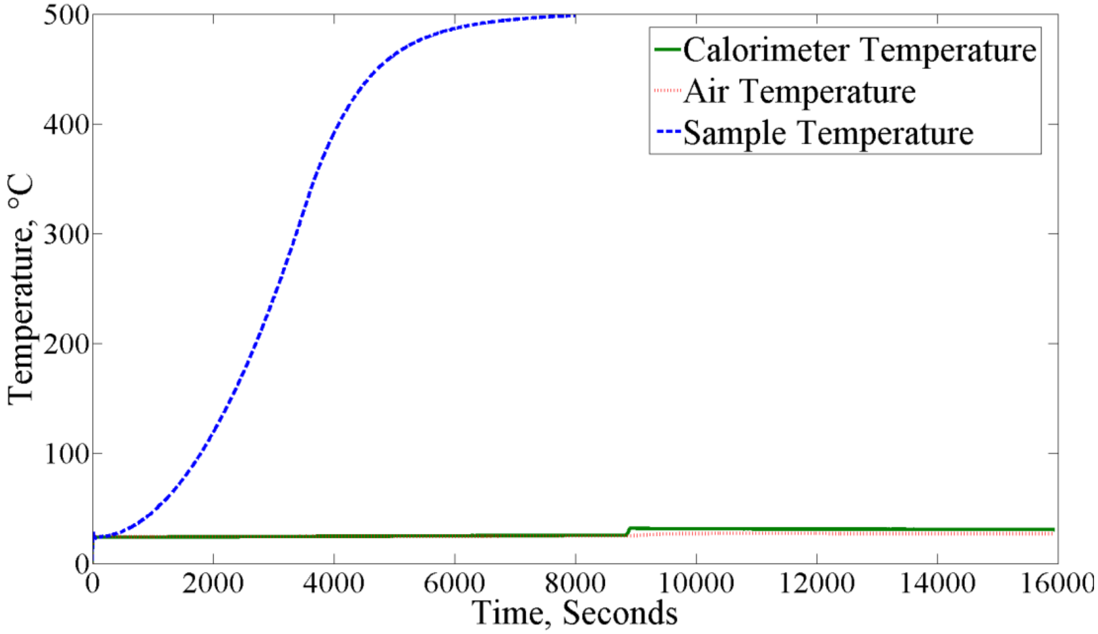

Figure 4. Example temperature trace from the entire experiment.

measured during the discharge process. The temperature recordings for the entire length of a typical experiment are shown in Figure 4. At around 9,000 seconds the EPCM sample was submerged into the calorimetry system and the temperature of the calorimeter began to increase.

Figure 5 shows a zoomed in trace of the calorimeter temperature after the time the EPCM sample was submerged, at which point the sample began to transfer all of its stored thermal energy to the calorimeter system, causing the temperature of the calorimeter to increase. At the equilibrium time, $t_{e,}$ the EPCM sample and the calorimeter had reached their equilibrium temperature. The equilibrium time varies depending on the size of the EPCM sample, the PCM being tested, and the charged temperature of the EPCM. To ensure that all calculations during the analysis were performed after equilibrium has occurred, only the last 3,000 seconds of the entire two hour (7,200 seconds) cooling process were used.

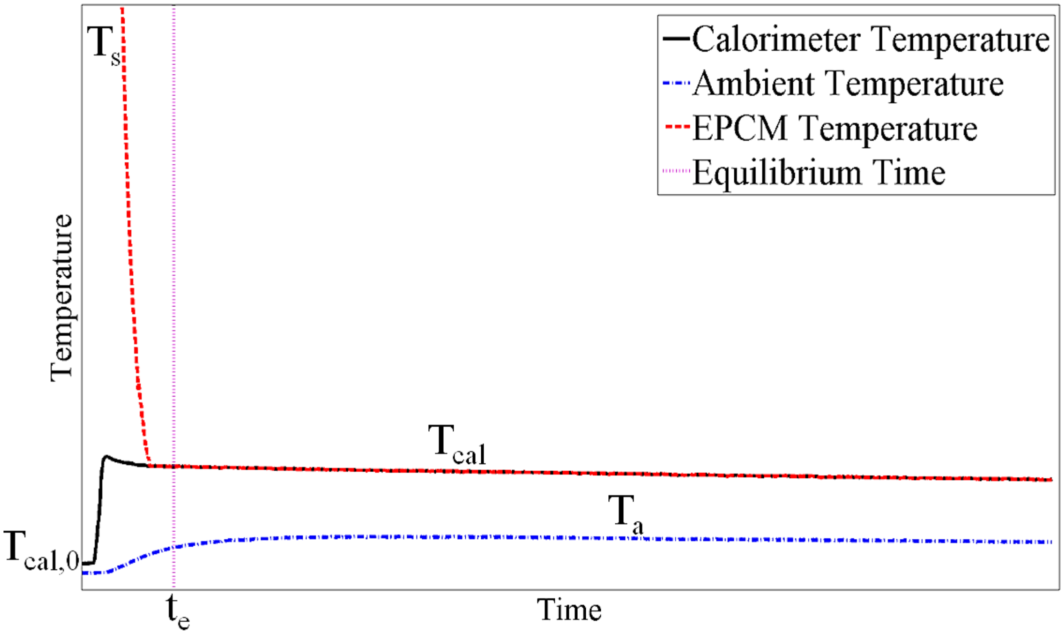

Figure 5. Temperature measurements during a typical calorimetry experiment

After the equilibrium time, both the temperature of the EPCM and calorimeter began to slowly decrease due to heat lost to the surroundings. By measuring the rate of the decline in temperature, the amount of heat loss was calculated and used to determine the theoretical equilibrium temperature that would have been reached if the system had no heat loss. Finally, using the initial temperature of the calorimeter and the theoretical equilibrium temperature, the amount of thermal energy transferred to the calorimetry system from the EPCM sample was calculated and compared to a theoretical value of the energy that was stored by the EPCM sample during the heating process.

2.3 Energy Analysis

The data recorded during each experiment was analyzed using MATLAB to determine the thermal energy stored by each EPCM sample, the energy transferred to the calorimeter during the experiment, and the percent difference between the two values [21] [22]. The equations governing the conservation of energy for the calorimetry system are:

$$Q_{EPCM,\exp} = Q_{cal} - Q_{loss} = m_{cal}\int_{T_{cal,0}}^{T_{cal}} c_{p,cal}\,dT - Q_{loss} \tag{1}$$

$$Q_{loss} = \int_{t_0}^{t} \dot{Q}_{net}\,dt = \int_{t_0}^{t} [-hA(T_{cal} - T_a) + \dot{Q}_{mixer}]dt \tag{2}$$

$$\begin{aligned} Q_{EPCM,theo} &= Q_{cap} + Q_{PCM} \\ &= m_{cap}\int_{T_{cal}}^{T_{s,0}} c_{p,cap}\,dT + m_{PCM}\int_{T_m}^{T_{s,0}} c_{p,PCM}^{l}\,dT + m_{PCM}LH_{PCM} + m_{PCM}\int_{T_{cal}}^{T_m} c_{p,PCM}^{s}\,dT \end{aligned} \tag{3}$$

where, m_{cal} is the mass of calorimeter (kg); $c_{p,cal}$ is the heat capacity of the calorimeter (J/kg·K); m_{cap} is the mass of the stainless less capsule (kg); $c_{p,cap}$ is the heat capacity of the encapsulation material as a function of temperature (J/kg·K); m_{PCM} is the mass of the PCM (kg); $c_{p,PCM}^{s}$ is the solid heat capacity of the PCM (J/kg·K); $c_{p,PCM}^{l}$ is the liquid heat capacity of the PCM (J/kg·K); LH_{PCM} is the latent heat of the PCM (J/kg); T_s is the sample temperature (K); T_{cal} is the temperature of the calorimeter (°C); T_a is the air temperature (°C); $T_{cal,0}$ is the initial calorimeter temperature (°C); $T_{s,0}$ is the initial sample temperature (K); and T_m is the melting temperature of the PCM (K) [14].

In order to calculate both the theoretical energy stored by the EPCM sample and the energy transferred to the calorimetry system, the equilibrium temperature that the EPCM sample and the calorimeter would have reached with zero heat loss is used.

However, in order to find the theoretical equilibrium temperature, the amount of heat loss from the system is needed. The heat lost to the surroundings varies with each individual experiment based on the initial room temperature and the temperature reached by the EPCM during heating. The final temperature of the EPCM sample after heating varies slightly because, while the furnace is set to a constant temperature for each experiment, the initial temperature of the sample when heating starts varies based on the room temperature at the time the experiment begins. The heat loss is responsible for the decrease in temperature of the calorimeter after equilibrium has been reached. Therefore by determining the rate at which the temperature of the calorimeter decreases during the experiment the heat loss from the system was calculated.

The rate at which heat is lost from the calorimeter requires a transient heat transfer analysis. While there are several ways to solve a transient heat transfer problem, the simplest is the method of lumped capacitance. Lumped capacitance assumes that the temperature difference inside the substance is negligible. The silicone oil that was used has a relatively high thermal conductivity so the temperature within the container of silicone oil should be constant with respect to radial distance and height. To verify that the temperature within the silicone oil was indeed constant and that the method of lumped capacitance could be utilized, several thermocouples were placed in the silicone oil at different locations and heights. The results of this test verified that the temperature across the container of silicone oil was indeed constant and therefore the method of lumped capacitance could be used.

From lumped capacitance, the temperature of the calorimeter at any time after the equilibrium time is represented by the following equation,

$$T_{cal} = (T_{cal,0} - T_a)\exp\left[\frac{-hA}{m_{so}c_p}t\right] + T_{cal,0} = a_1\exp\left[\frac{-a_2}{m_{so}c_p}t\right] + a_3 \qquad \textbf{(4)}$$

where $T_{cal,\ 0}$ is the initial calorimeter temperature; T_a is the temperature of the surroundings; h is the heat transfer coefficient; A is the surface area; m_{so} is the mass of the silicone oil; c_p is the effective heat capacity of the system; and t is the time at which the temperature is desired. While some of the constants in equation 4 are unknown, they can be determined by curve-fitting the recorded temperature of the calorimeter over the course of the experiment. Then, by differentiating the equation found for temperature, the total heat loss rate in the system, including the now cooled EPCM sample, was determined by using the following equation;

$$\dot{Q}_{net} = (m_{PCM}c^s_{p,PCM} + m_{cap}c_{p,cap} + m_{cal}c_{p,cal}) \times \left[\left(\frac{-a_2}{mc_p}\right)\left(a_1\exp\left(\frac{-a_2}{mc_p}\right) * t\right)\right] \qquad \textbf{(5)}$$

Additionally, as seen in equation 2, $\dot{Q}_{net}$ is also equal to the rate of heat lost from the system to the surroundings through convection plus the heat input to the calorimeter by the mixer. By plotting the heat rate determined from equation 5 versus the difference in temperature between the calorimeter and the surrounding air, the two unknown coefficients in equation 2, hA and $\dot{Q}_{mixer}$, are determined. Knowing these coefficients, the cumulative heat loss from the calorimeter (Q_{loss}) at any time is calculated by integrating $\dot{Q}_{net}$ from the initial time the sample was submerged in the system, t_0, to any subsequent time t later.

The calculated value of heat loss was then used to determine the theoretical equilibrium temperature the EPCM sample and calorimeter should have reached by adding it to the calculated enthalpy of the calorimeter and the sample EPCM at any time during the experiment. This total amount of energy is then divided by the mass of the calorimeter system and EPCM sample to determine the theoretical equilibrium temperature by using the following equation;

$$T_{theo} = \frac{\left(m_{cal}c_{p,cal} + m_{PCM}c_{p,PCM}^{s} + m_{cap}c_{p,cap}\right) * T + Q_{loss}}{\left(m_{cal}c_{p,cal} + m_{PCM}c_{p,PCM}^{s} + m_{cap}c_{p,cap}\right)} \qquad \textbf{(6)}$$

The temperature T in the above equation is calculated by using equation 4. The theoretical temperature was then used as T_{cal} in equations 1 and 3 to calculate the theoretical and experimental enthalpies.

2.4 System Calibration

Not only is the heat that was lost to the surroundings needed to calculate the amount of energy that was transferred to the calorimeter from the EPCM sample, but also the effective heat capacity of the calorimeter, which was unknown. The heat capacity of the calorimeter system cannot simply be taken as that of the silicone oil alone because it only accounts for 83% of the mass of the system. The other 17% of the system consists of the metal container (0.6kg), the foam insulation (0.242kg), and the mixer blade (0.0966kg). These three components each have their own heat capacity and contribute to the calorimeter's storage ability.

The heat capacity of the calorimeter system was determined by calibrating the system using two solid standard stainless steel 304 samples. The two samples had different dimensions and masses which caused a range of temperature increases in the calorimeter. The specifications of the two samples are listed in Table 1. Stainless steel 304 was chosen because of its well documented thermal properties and high melting point, allowing for the samples to only store sensible heat over a wide range of temperatures. The thermal properties of stainless steel are listed in Table 2 [23]. However, the heat capacity of stainless steel varies considerably over the temperature range of interest. Therefore, an equation for heat capacity as a function of temperature was determined from the data listed in Table 2 and integration over the applicable temperature range was employed to determine the amount of thermal energy stored in the stainless steel samples.

Table 1. Specifications of Stainless Steel Calibration Samples

	Mass of Sample (g)	Size (Diameter × Height)
Sample 1	834.3	3.81 cm × 10.16 cm
Sample 2	185.1	2.53 cm × 4.64 cm

Table 2. Thermal properties of stainless steel 304 [23]

Melting Point (°C)	Heat Capacity (J/kg K)						
1397	300 K	400 K	600 K	800 K	1000 K	1200 K	1500K
	477	515	557	582	611	640	682

By preheating the stainless steel samples to various temperatures, it was possible to obtain the energy transferred to the calorimetry system over a range of temperatures. From the energy transferred to the system, the heat capacity of the calorimeter system as a function of temperature was determined by using the following equation;

$$c_{p,cal} = \frac{Q_{EPCM,theo}}{m_{cal} T_{cal}} \tag{7}$$

where m_{cal} is the mass of the calorimeter, approximately 5.3kg; $Q_{EPCM,\ theo}$ is energy stored by the stainless steel sample; and T_{cal} is the average temperature of the calorimeter, i.e., the average of initial calorimeter temperature and the theoretical equilibrium temperature. The results of the calibration tests, depicted in Figure 6, were well represented by the following equation, in the operational range of 25-60 °C

$$c_{p,cal} = 2.5297 \times T_{cal} + 1312.6 \tag{8}$$

where $c_{p,\ cal}$ is the effective heat capacity of the entire calorimeter system in J/kg K and T_{cal} is the calorimeter temperature in °C.

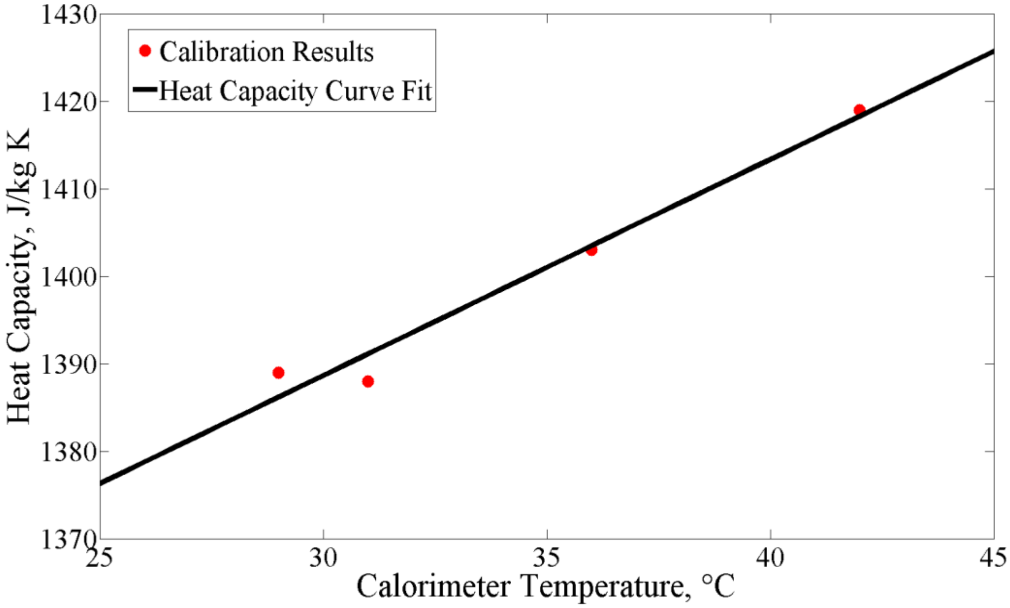

Figure 6. Calibration Results

2.5 System Verification

After calibration of the effective heat capacity of the system was completed, the overall performance of the calorimeter was determined by performing several verification tests. The calorimeter's ability to accurately measure the sensible heat stored by a sample was found by using the same stainless steel samples used for calibration. The calorimeter's accuracy for measuring the energy storage of a sample that stores both sensible and latent heat was determined by using a 2.54cm diameter by 5.08cm tall Al-stainless steel EPCM sample with 42.45g of Al.

Following the same experimental procedure outlined above, the stainless steel samples were heated to several preselected temperatures, 256°C, 390°C, 480°C, and 555°C, while the Al-stainless steel EPCM was heated to 720°C. The theoretical equilibrium temperature was determined for each experiment and then used to calculate the theoretical energy stored in the sample. Similarly, the energy transferred to the calorimeter from the sample was calculated by integrating the equation for heat capacity found through calibration from the initial temperature of the calorimeter to the theoretical equilibrium temperature. The percent difference between the theoretical and experimental enthalpies was calculated using the following equation;

$$\%Difference = \frac{Q_{EPCM,theo} - Q_{EPCM,\exp}}{Q_{EPCM,theo}} \times 100 \qquad \textbf{(9)}$$

where a positive error indicates that theoretically the sample should store more energy that it did experimentally, and a negative error means that sample did experimentally better than expected. Since there are small errors in the measurement of both the initial sample temperature and the calorimeter temperature, both positive and negative error can occur.

The results of the verification tests for both sensible and latent heat storage are tabulated in Table 3. It is shown that the energy balance between the theoretical and experiential energy storage was satisfied with less than ±2% error, lending confidence to both the experimental method and calorimetry measurements used to determine the performance of candidate PCMs.

Table 3. Results of verification experiments

Material	Sample #	Charged Temperature (°C)	Theoretical Equilibrium Temperature (°C)	Theoretical Energy Stored (kJ)	Measured Energy Stored (kJ)	Error (%)
Stainless Steel	1	256	37.7	94.1	94.7	-0.64
	1	390	46.1	153.0	152.6	0.26
	2	480	31.7	44.8	44.5	0.70
	1	555	56.7	228.0	227.4	0.26
Al	1	720	32.2	76.1	74.6	1.9
	1	700	33.0	74.7	76.0	-1.7

2.6 Conclusions for the Immersion Calorimetry System

A conventional immersion calorimeter was specially designed for use in the testing of candidate PCMs for use in high temperature TES at CSP plants. The calorimeter system that was designed consisted of an insulated container of approximately 4.5kgs of silicone oil that was further insolated using foam board boxes. The effective heat capacity of the calorimeter was determined through calibration by using standard stainless steel samples. The results of calibration showed that 90% of the effective heat capacity of the system was from the silicone oil.

Additionally, by using the standard stainless steel samples for sensible heat storage and an Al EPCM sample for latent heat storage, the accuracy of the calorimeter was evaluated by performing an energy balance analysis between the theoretical storage capability of each sample and what was experimentally measured. From the results of the verification tests it was determined that the overall accuracy of the designed calorimeter’s ability to measure the energy stored in the EPCM sample was within ±2%. These results make not only the calorimeter's ability to measure the thermal energy stored in an EPCM sample credible but also the experimental method used.

CHAPTER 3

SODIUM CHLORIDE - STAINLESS STEEL EPCM TESTING

Sodium chloride is a good candidate PCM for high temperature TES because of its high melting point, 800°C, and its high latent heat of fusion, 430kJ/kg. The use of NaCl as a PCM would increase the temperature range in which TES can be utilized to 850°C, well above the 600°C required by CSP power plants. After much consideration it was decided to use stainless steel 304 as the capsule material for the NaCl EPCM samples and two NaCl-stainless steel EPCM samples were made [17] [18]. Each capsule had a diameter of 2.54cm and a height of 5.08cm. The masses of PCM in the two NaCl-stainless steel EPCM samples were 27.0g and 26.6g.

To evaluate the storage capacity of the NaCl-stainless steel EPCM samples, they were repeatedly tested in the calorimetry system. The storage capacity was examined after multiple short-term cycles and after prolonged exposure to high temperatures. Additionally, once testing was complete the NaCl-stainless steel EPCM samples were examined to ensure that there was no reaction between the PCM and the capsule that would result in a loss of storage capacity over time. The thermodynamic properties of NaCl were needed for the calculation of the theoretical energy storage of the NaCl-EPCM samples. However, the properties of NaCl in the working temperature range (25°C – 850°C) were either not reported or were inconsistent. Therefore the calorimetry system was used to determine both the heat capacities and the latent heat of NaCl.

3.1 Properties of NaCl PCM

In order to evaluate the storage capacity of the NaCl-stainless steel EPCMs the thermodynamic properties of NaCl were needed. Since accurate properties were not reported in literature, these properties were determined using the calorimetry system. First the solid heat capacity was determined, followed by the liquid heat capacity, and finally the latent heat of fusion was calculated [24]. The solid heat capacity of NaCl was determined by heating the NaCl EPCM sample to a temperature slightly below the 800°C melting point of NaCl and then immersing the sample in the calorimeter. By performing an energy balance analysis, as described above in section 2.3, the average solid heat capacity from ambient temperature to 800°C was determined with the following equation;

$$c_{p,PCM}^{s} = \frac{Q_{EPCM,\exp} - m_{cap} c_{cap} \left(T - T_{cal}\right)}{m_{PCM} \left(T - T_{cal}\right)} \tag{10}$$

where $Q_{EPCM,\ exp}$ is the calculated enthalpy of the calorimeter from the experiment; m_{cap} is the mass of the stainless steel capsule; c_{cap} is the solid heat capacity of stainless steel; m_{PCM} is the mass of the PCM; T is the initial temperature of the EPCM (approx. 800°C) when it is submerged in the calorimeter; and T_{cal} is the temperature of the calorimeter with zero heat loss.

The liquid heat capacity was determined by heating the NaCl EPCM sample to two different temperatures above the melting point of NaCl and calculating the experimental energy stored in the EPCM sample for both temperatures. The liquid heat capacity was then determined by dividing the difference in energy stored in the

PCM by the mass of the PCM and the temperature difference between the experiments;

$$c^{l}_{p,PCM} = \frac{\Delta Q_{PCM}}{m_{PCM}\left(T_2 - T_1\right)} = \frac{\Delta Q_{EPCM} - m_{cap}c_{p,cap}\left(T_2 - T_1\right)}{m_{PCM}\left(T_2 - T_1\right)} \qquad \textbf{(11)}$$

where T_2 and T_1 are the temperatures of the respective experiments. Finally, after both the solid and liquid heat capacities were determined the latent heat of fusion was calculated, using equation 12, by subtracting the energy stored in the capsule and the sensible heat storage of the PCM from the total energy stored in the EPCM from either of the two experiments used to calculate the liquid heat capacity.

$$LH_{PCM} = \frac{Q_{EPCM} - m_{cap}c_{p,cap}\left(T_{s,0} - T_{cal}\right) - m_{PCM}c^{s}_{p,PCM}\left(T_m - T_{cal}\right) - m_{PCM}c^{l}_{p,PCM}\left(T_{s,0} - T_m\right)}{m_{PCM}} \qquad \textbf{(12)}$$

The measured values for the latent heat of fusion and both the solid and liquid heat capacities were compared to values reported by Janz, G.J. et al., 1979 [25] and Chase, M.W. 1998 [26] in Table 4. While the calculated liquid heat capacity was in good agreement with the values presented in literature, both the solid heat capacity and latent heat were considerably different. However, it is hard to compare values since the reference temperature between the calorimetry experiments and those presented in literature were different.

Table 4. Measured thermodynamic properties of sodium chloride

Solid Heat Capacity (kJ/kg·K)	Liquid Heat Capacity (kJ/kg·K)	Latent Heat (kJ/kg)	Reference
0.931	1.215	430	Present Work [24]
---	1.20	481	Janz, G.J. et al., 1979 [25]
0.987	1.19	---	Chase, M.W., 1998 [26]

These thermodynamic properties allow for the calculation of the theoretical energy storage of the NaCl EPCM sample which was then compared to the measured energy stored in the sample during the calorimetry tests. Additionally, based on these properties for a 100 degree temperature range centered on the melting point of NaCl, 80% of the energy stored by the EPCM is from latent heat storage.

3.2 Performance of NaCl-stainless Steel EPCM after Short-Term Cycling

To evaluate the performance of NaCl as a PCM for use in high temperature TES, two NaCl-stainless steel EPCM samples were fabricated with a diameter of 2.54cm and a height of 5.08cm and masses of 27.0g and 26.6g. The two samples were then tested using the calorimetry system to determine the amount of thermal energy stored by each sample. The typical length of each NaCl-stainless steel EPCM calorimetry experiment was 2.1×10^4 seconds, or about 6 hours. The temperatures that were recorded for the entire experiment are shown in

Figure 7.

The dashed line shows the heating of the NaCl-stainless steel EPCM from room temperature to 850°C at a rate of 500°C per hour. At close to 6,000 seconds the surface of the sample had reached the desired charging temperature and remained relatively constant during the time the sample is held at 850°C to ensure all the of the PCM was melted. The solid line shows the temperature of the calorimeter for the entire 6-hour experiment. Due to electrical noise caused by the furnace a rolling average was used to smooth the data. Before the NaCl-stainless steel EPCM is submerged, the temperature of the calorimeter remained at a constant temperature (26°C).

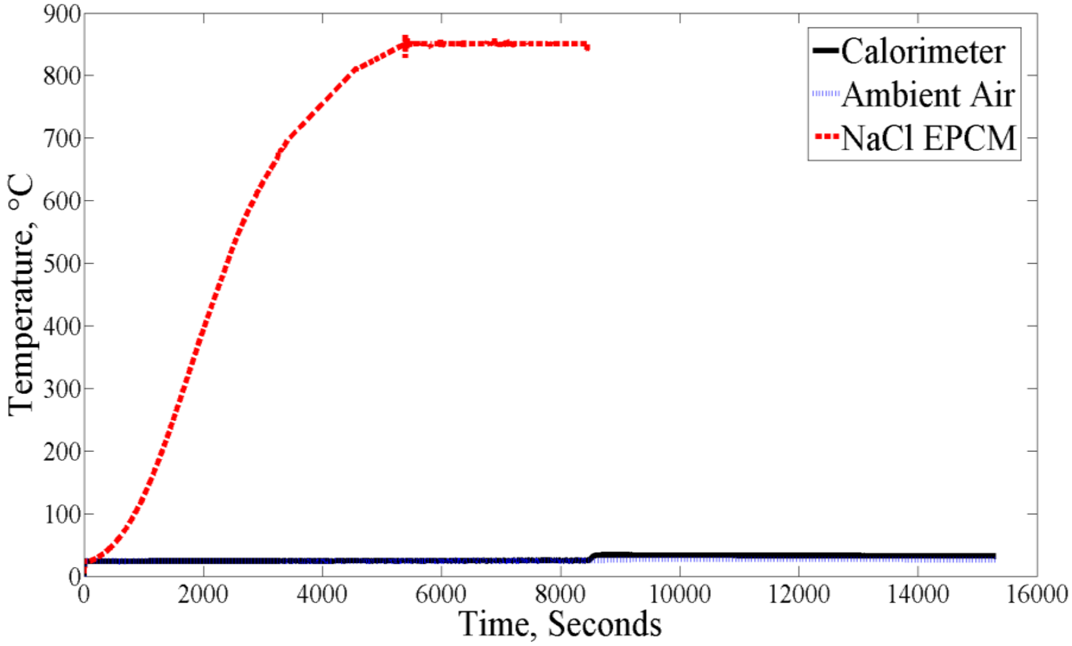

Figure 7. Temperature recordings for the entire length of a typical NaCl-stainless steel EPCM calorimeter experiment

At a time of approximately 1.33×10^4 seconds into the experiment (~4 hours) the sample was removed from the furnace and submerged into the calorimeter, at which point the temperature of the calorimeter began to increase. A zoomed-in figure of the temperature of the calorimeter from the time the NaCl-stainless steel EPCM sample was submerged until cooling was complete (~2 hours later) is shown in Figure 8. The temperature of the calorimeter increased from room temperature, 26°C, to a peak temperature of 34.6°C, after which the temperature of the calorimeter began to decrease due to heat lost to the surroundings until it reached a final temperature of 32.5°C.

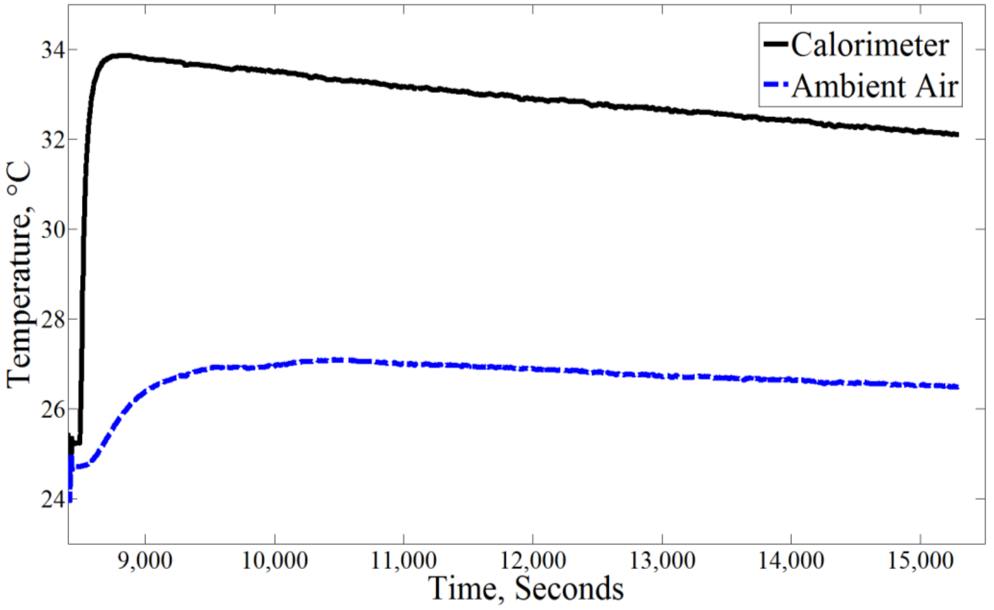

Figure 8. Expanded trace of calorimeter and ambient temperatures for NaCl EPCM cooling

The recorded data for the calorimeter temperature, the ambient air temperature, and the sample temperature were used to determine the heat that was lost from the system during each experiment and the theoretical equilibrium temperature the calorimeter would have reached without heat loss. The equilibrium temperature was then used to calculate the experimental energy stored in the EPCM sample, using equation 1. The thermodynamic properties of NaCl, determined by the calorimeter, were used to determine the theoretical energy storage for the NaCl EPCM, using equation 3, and to compare it to the experimental value to evaluate the performance of NaCl as a PCM for high temperature TES.

The results for all calorimetry testing of the two NaCl-stainless steel EPCM samples, including a comparison of the experimental and theoretical energy storage, is presented in Table 5. During the initial thermal cycle the two NaCl-stainless steel EPCM samples underwent a complete phase change and the error between the theoretical and experimental energy stored was 1.1% for sample 1 and -0.61% for sample 2, both values falling well within the ±2% accuracy of the calorimeter. Additionally, the results in Table 5 show that the storage capacity of NaCl does not diminish with repeated short-term thermal cycling (~6 hour cycles) as the agreement for all the cycles remained within ±2% and did not trend in one direction.

Table 5. Energy stored in NaCl in repeated thermal-cycles [24]

Sample No.	Thermal Cycle	Charged Temperature (°C)	Discharged Temperature (°C)	Theoretical Energy in NaCl EPCM (kJ)	Measured Energy in NaCl EPCM (kJ)	Error (%)
1	1	830	30	65.0	64.3	1.1
	2	830	33	64.9	65.1	-0.31
	3	850	33	66.0	65.9	0.15
2	1	850	30	65.9	66.3	-0.61
	2	850	32	65.7	64.8	1.4
	3	850	30	65.8	65.1	1.1

3.3 Performance of NaCl-Stainless Steel EPCM after Long-Term Cycling

Although the NaCl-stainless steel EPCM samples did not show any deterioration in storage capacity after repeated short-term cycling, their performance after long-term exposure to high temperatures was also studied to see if any loss of capacity would occur. The NaCl-stainless steel EPCM was heated to 850°C and held at that temperature for 1,000 hours. The sample was then re-tested using the calorimetry system to see if the long-term exposure to high temperatures had any effect on the thermal storage capabilities of the NaCl-stainless steel EPCM. The results of these calorimetry experiments are summarized in Table 6. The average error of the experiments after the long-term cycling was close to -2%, which is within the ±2% accuracy of the calorimetry system. It was therefore concluded from these results that the NaCl-stainless steel EPCM did maintain its storage capacity after long-term exposure to high temperatures.

Table 6. Energy stored in NaCl EPCM sample 1 after high-temperature exposure

Thermal Cycle	Exposure at 850 °C (hr)	Theoretical Energy in NaCl EPCM (kJ)	Measured Energy in NaCl EPCM (kJ)	Error (%)
1	1,000	66.3	68.0	-2.6
2	1,000	66.0	67.3	-2.0
3	1,000	65.3	66.7	-2.1
4	1,000	66.1	67.8	-2.6

After the calorimetry testing of the NaCl-stainless steel EPCM samples was completed, a sample was further examined for any potential reaction between the stainless steel capsule and the NaCl PCM that did not show up in the calorimetry experiments by sectioning the sample and taking micrographs. The micrographs in Figure 9 show the inside edge of the capsule, which was exposed to the molten NaCl, at two different locations. The dark region near the top of the micrograph is the mounting material used during preparation, while the light region is the stainless steel encapsulation material. It was concluded that the sample experienced either no corrosion or uniform corrosion because the interface surface appears to be flat without any pitting. Uniform corrosion would mean that the stainless steel surface in contact with the molten NaCl corroded in such a way that pitting corrosion and grain boundary corrosion was negligible compared to the overall corrosion of the capsule [24].

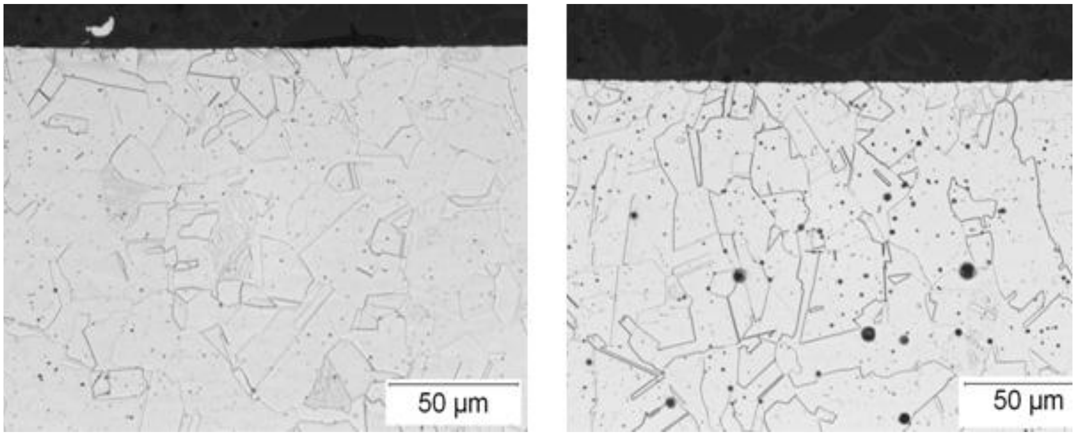

Figure 9. Light optical micrographs of the cross section of the surface in contact with NaCl EPCM after thermal cycling for 1000 hours. [24]

However, these capsules were never designed for extensive corrosion testing, so an accurate measure of the corrosion rate is beyond the scope of this work. Although there was potentially some reaction between the stainless steel capsule and the NaCl PCM, NaCl-based EPCMs still have good potential for thermal energy storage at high temperatures.

3.4 Conclusions for NaCl-Stainless Steel EPCM Performance

Based on the results of the calorimetry testing of NaCl-stainless steel EPCMs presented in this chapter, it was concluded that NaCl can be used as a high temperature phase change material for the storage of thermal energy in the range of 850°C, making it suitable for use in CSP systems. From the determined thermodynamic properties of NaCl, it was calculated that 80% of the thermal energy stored by NaCl for a 100°C temperature range centered on the salt’s melting point can be attributed to the latent heat of fusion. The results of all the calorimetry testing on the NaCl-stainless steel EPCM samples were within the ±2% accuracy of the calorimeter system. Additionally, the samples did not show any discernible decrease in the storage capacity after repeated short-term cycles.

The NaCl-stainless steel EPCM samples were also exposed to high temperatures (850°C) for an extended period of time (1,000 hours). After this long-term exposure the NaCl-stainless steel samples were retested, and since the results of these calorimetry tests were also within the ±2% system accuracy it was concluded that no loss of storage capacity occurred. However, micrographs of the NaCl-stainless steel EPCM taken after all testing was completed indicated the presence of at least some level of reaction between the NaCl PCM and the stainless steel capsule. Therefore it is concluded that while NaCl is a good choice of PCM for use in high temperature TES, it should be encapsulated in a less reactive material to ensure no loss of storage capacity will occur over the life of the EPCM.

CHAPTER 4

ALUMINUM - STAINLESS STEEL EPCMS

One of the issues that can arise when using salts as the PCM material for TES is their general low thermal conductivity. The low thermal conductivity of solid salts increases the total heat transfer time required to charge (melt) or discharge (solidify) the entire PCM. This was the main problem encountered when using a large tank of PCM with internal heat transfer tubes, particularly during discharge of the system. While encapsulating the PCM does reduce the total heat transfer time, using a metal PCM over a salt would further reduce the total charge and discharge times.

The thermodynamic properties of aluminum make it a good choice of a metal PCM for the use in high temperature TES. The high 660°C melting point of Al would allow for thermal energy storage to occur at temperatures above 700°C. Additionally, the high latent heat of fusion for Al, 397kJ/kg, would increase the percentage of heat stored in the capsule that is from latent heat storage. Although there was the potential for a reaction between the capsule and PCM, it was decided to use stainless steel 304 to encapsulate the Al PCM. Three Al-stainless steel EPCM samples were fabricated with masses of 42.45g, 42.52g, and 42.40g and dimensions of 2.54cm by 5.08cm. The Al-stainless steel EPCM samples were repeatedly tested in the calorimeter to evaluate their storage capacity after both short and long-term exposure to high temperatures.

4.1 Properties of Al PCM

The thermodynamic properties of Al that were needed for the calculation of the amount of thermal energy stored by the Al-stainless steel EPCM samples were determined from literature and are listed in Table 7 [27]. While the liquid heat capacity of Al remains constant over the working temperature range, the solid heat capacity varied by 355J/kg K from 904J/kg K at room temperature to 1259J/kg K just before melting occurs at 660°C. Therefore integration was used during the calculation of the theoretical energy stored by the sample to obtain accurate results.

Table 7. Thermodynamic properties of Al

Solid Heat Capacity (kJ/kg·K)					Liquid Heat Capacity (kJ/kg·K)	Latent Heat (kJ/kg)
300K	500K	700K	900K	933K	1.177	397.3
0.904	1.000	1.085	1.225	1.259		

Based on these thermodynamic properties of Al, 79% of the total energy stored by an Al EPCM for a 100 degree temperature swing centered on the 660°C melting point of Al can be attributed to the latent heat of fusion. Additionally, since the thermal conductivity of the PCM effects the charge and discharge times, the thermal conductivity of Al (237W/m K) only makes it a stronger candidate PCM. By comparing the thermal conductivity of Al to that of NaCl (6.5W/m K), which was studied as a PCM in the previous chapter, it was determined that the thermal conductivity of Al is 36.5 times larger than that of NaCl. The higher thermal conductivity of Al would result in faster conduction of the heat supplied to surface of the capsule reaching the center of the PCM, reducing the total charge or discharge time for the capsule.

4.2 Performance of Al-Stainless Steel EPCM after Short-Term Thermal Cycling

The performance of Al as a PCM for use in high temperature TES was evaluated by making and testing three Al-stainless steel EPCM samples. The three cylindrical EPCM samples had masses of 42.45g, 42.52g, and 42.40g. Using the calorimeter the total amount of thermal energy stored in each sample was calculated and compared to the theoretical storage based on the thermodynamic properties of Al. During each calorimeter test the Al-stainless steel EPCM sample was heated in a 720°C furnace. The length of the short-term cycle experiments performed for Al had a length of around 16,000 seconds (~5 hours). The temperature of the calorimeter and ambient air were recorded for the entire length of the experiment, while the temperature of the Al-stainless steel EPCM sample was recorded until it was submerged into the calorimeter. These temperature recording are presented in Figure 10.

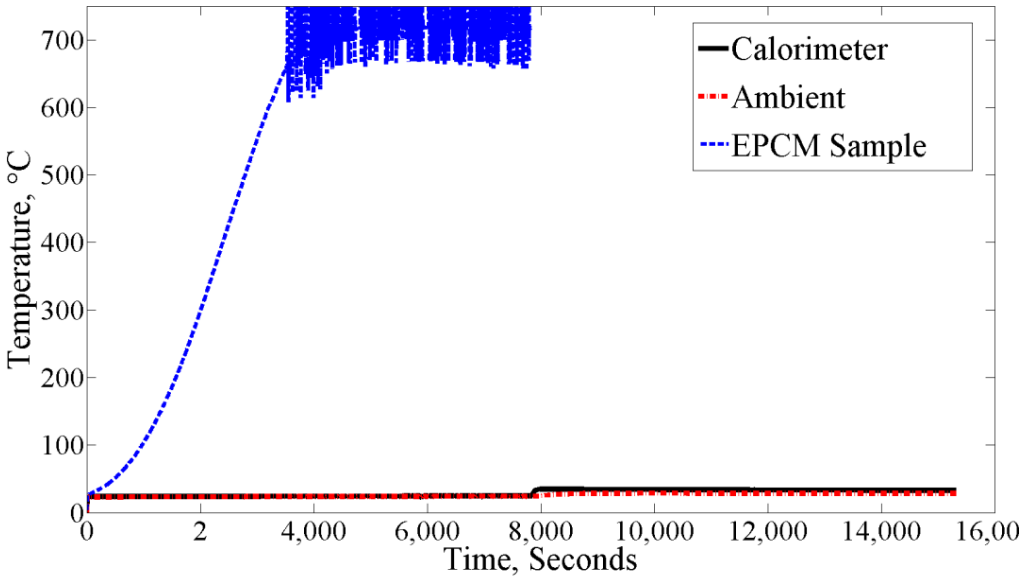

Figure 10. Sample temperature recordings during Al EPCM testing

The dashed blue line in Figure 10 shows the heating of the Al-stainless steel EPCM from room temperature to around 720°C. The rate at which the electric furnace supplied heat was 700°C per hour. From Figure 10 it is seen that once the temperature of the sample reached approximately 650°C the measurements of the thermocouples began to fluctuate. Additionally, as the temperature increased to 720°C, the rate of these fluctuations increased. After testing the thermocouples in the furnace without a sample it was concluded that the fluctuations were caused by electrical noise from the furnace due to the stopping of the fluctuations when the furnace was turned off, Figure 11. To eliminate the noise and obtain accurate readings for the initial sample temperature, the furnace was turned off for about half a minute, to ensure the temperature readings were steady before the thermocouples were disconnected.

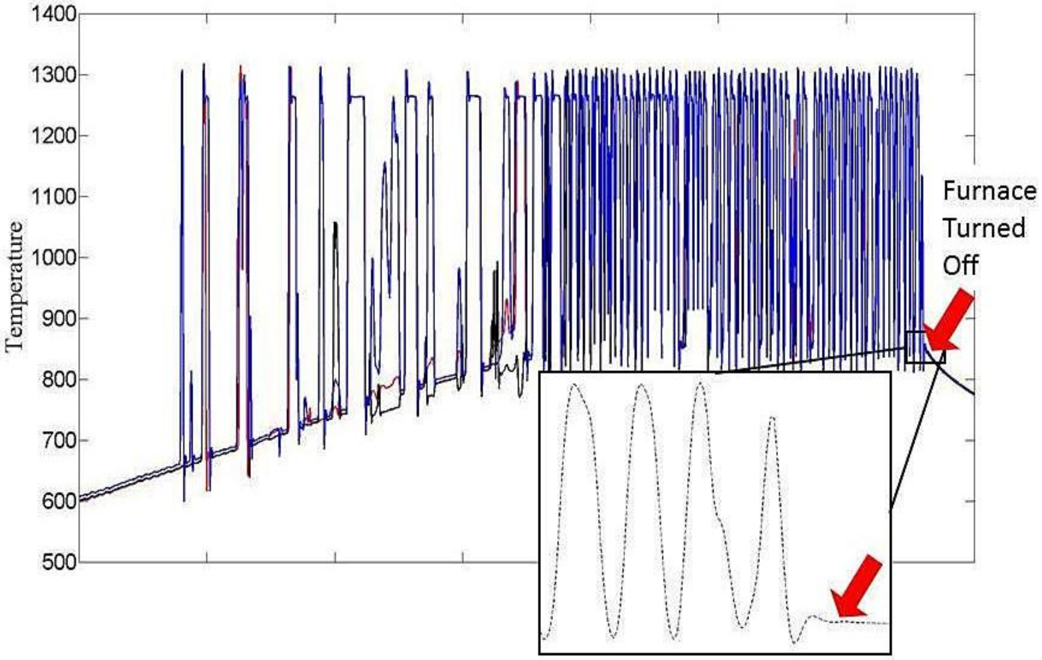

Figure 11. Fluctuations in temperature readings caused by electrical noise

For all of the calorimeter experiments involving Al, the furnace was set to a maximum temperature of 720°C. However, depending on the initial temperature of the Al sample, the final temperature the sample reached at the end of the heating process varied from 700°C to 715°C. After approximately 8,000 seconds (2 hours) the Al-stainless steel EPCM sample was removed from the furnace and dropped into the calorimeter. The temperature recordings of the calorimeter and ambient air for the length of the cooling process are presented in Figure 12. The temperature of the calorimeter during the entire heating process had remained a constant 25°C and increased to a maximum temperature of 35°C once the sample was submerged. After that point the temperature of the calorimeter began to decrease at a rate proportional to the rate of heat lost from the system to the surroundings.

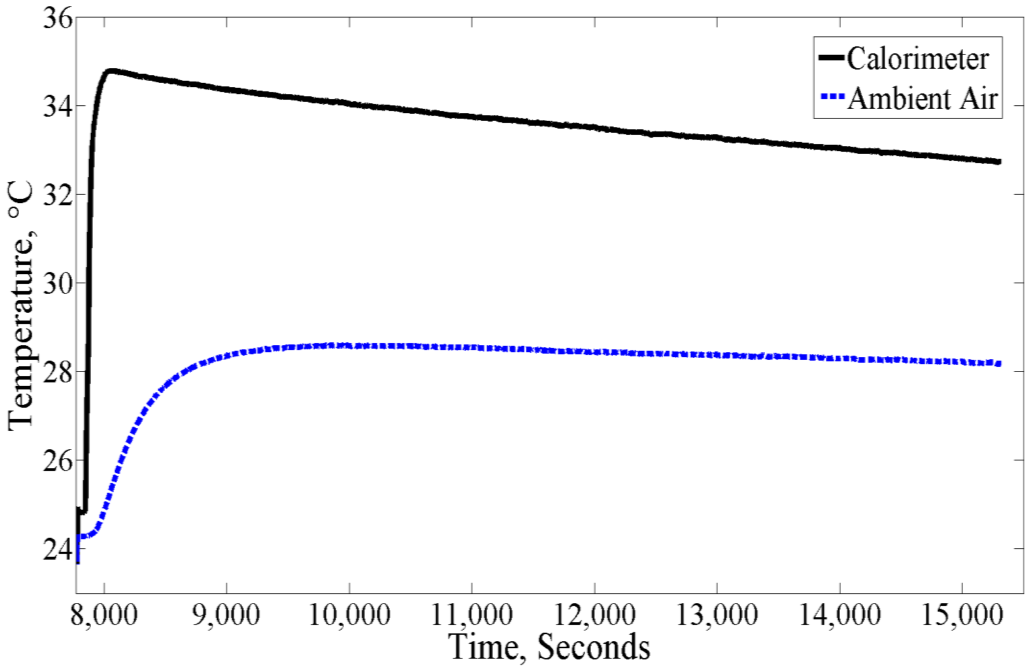

Figure 12. Sample calorimeter and ambient air temperatures during Al EPCM testing

The measured temperatures were used to determine the rate of heat loss from the system which was then integrated to find the total heat loss that occurred during the two hour cooling of the Al-stainless steel EPCM sample. The theoretical temperature that the Al-stainless steel EPCM and calorimeter should have reached in equilibrium was determined by correcting the measured energy in the system for heat loss. Once the equilibrium temperature was known both the theoretical and experimental thermal energy stored in the Al-stainless steel EPCM were calculated and compared to determine if Al makes a good PCM for use in high temperature TES.

The results of the Al-stainless steel EPCM calorimetry testing are presented in Table 8. During the initial thermal cycle, the entire mass of Al PCM in the EPCM sample underwent a phase change because the Al-stainless steel EPCM sample had yet to be exposed to high temperatures, so alloying between the two metals had yet to occur, if it were to occur at all. The results of all subsequent thermal cycles were compared to the results of the initial cycle to see if there was a loss of storage capacity within the Al-stainless steel EPCM sample. The percent differences between the theoretical and experimental energy stored in the three Al-stainless steel EPCM samples during the initial thermal cycle were 0.26%, 1.43%, -0.09% for samples one, two, and three, respectively. The results of the short-term thermal cycling (~5 hours) tests performed on the Al-stainless steel EPCM samples showed that there was no loss of storage capacity in the samples after repeated thermal cycles as the percent difference between theoretical and experiment energy storage of the samples remained within the ±2% accuracy of the calorimetry system.

Table 8. Energy stored in Al in repeated thermal-cycles

Sample No.	Thermal Cycles	Charged Temperature (°C)	Equilibrium Temperature (°C)	Theoretical Energy Stored(kJ)	Measured Energy Stored (kJ)	Error (%)
1	1	710	32.8	75.5	75.3	0.26
	2	710	32.8	75.3	74.1	1.59
	3	710	33.2	75.7	77.1	-1.85
	4	710	33.3	75.5	76.0	-0.66
2	1	748	35.3	79.2	78.1	1.43
	2	712	34.8	75.8	75.1	0.86
	3	702	35.2	74.9	74.5	0.47
3	1	705	35.2	74.3	74.4	-0.09
	2	704	35.2	74.2	74.4	-0.21
	3	714	35.1	75.2	75.1	0.08

4.3 Performance of Al-Stainless Steel EPCM after Long-Term Thermal Cycling

While the Al-stainless steel EPCM samples did not show a reduction in storage capacity with repeated short-term thermal cycles, the effect of long-term exposure to high temperatures on the storage capacity of the Al-stainless steel EPCM samples was also examined. The Al-stainless steel EPCM samples were held in a furnace at 720°C for 500 hours. After the 500 hours exposure to 720°C was complete the storage capacity of the Al-stainless steel EPCM samples were evaluated using the calorimetry system. The results of the calorimetry testing performed after long-term exposure to high temperatures are presented in Table 9. The results of the post long-term calorimetry testing for sample one showed an average decrease in storage capacity of 4.1%.

Table 9. Energy stored in Al EPCM after high-temperature exposure

Sample	Thermal Cycle	Exposure at 720 °C (hrs)	Charged Temperature (°C)	Theoretical Energy Storage (kJ)	Measured Energy Storage (kJ)	Error (%)
1	1	500	704	74.9	72.4	3.3
1	2	500	715	75.9	72.1	4.9

To further study the decrease in storage capacity after long-term exposure to high temperatures, the first Al-stainless steel EPCM sample was exposed to 720°C for an additional 500 hours, bringing the total exposure time for sample 1 to 1,000 hours. The sample was then tested in the calorimeter to see if a further decrease in storage capacity occurred or if the reduction remained a constant 4%. The results of these additional tests on the Al-stainless steel sample 1 after 1,000 hours of exposure to

720°C are shown in Table 10. The reduction in storage capacity increased to 10.4% after exposure to high temperatures for 1,000 hours. Figure 13 shows a graphical representation of the loss of storage capacity experienced by the Al-stainless steel EPCM samples.

Table 10. Energy stored in Al EPCM after high-temperature exposure for 1,000 hours

Sample	Thermal Cycle	Exposure at 720 °C (hrs)	Charged Temperature (°C)	Theoretical Energy Storage (kJ)	Measured Energy Storage (kJ)	Error (%)
1	1	1,000	714	75.9	67.9	10.5
1	2	1,000	717	76.1	68.3	10.3

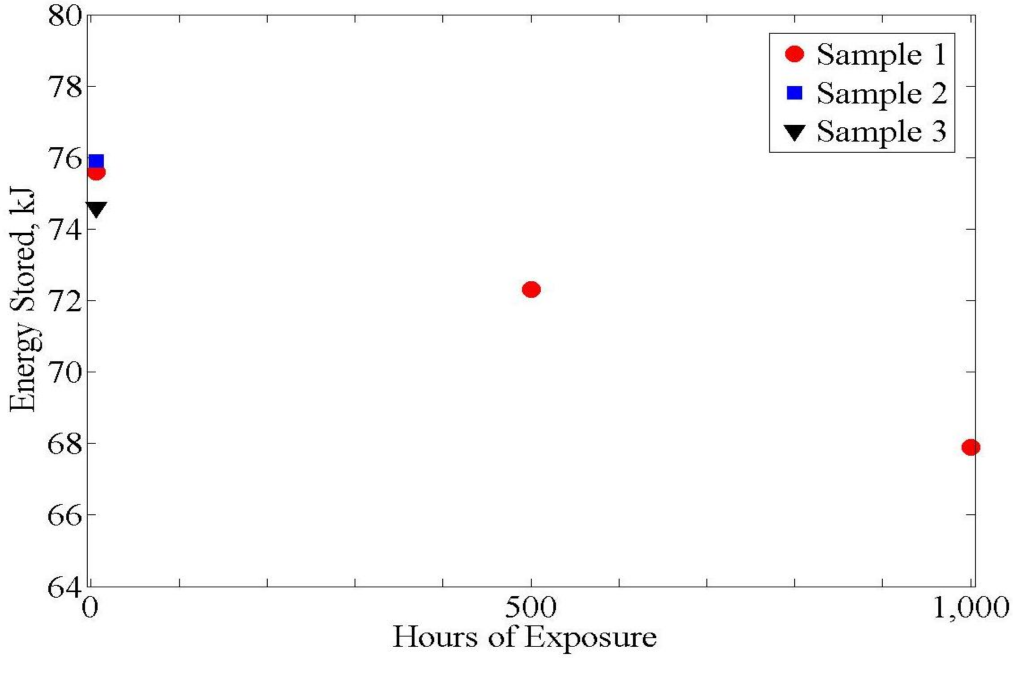

Figure 13. Loss of storage capacity experienced by Al-stainless steel EPCM samples

Although there was a loss of storage capacity of the Al-stainless steel EPCM, Al-based EPCM are still a good choice for TES at high temperatures for use in CSP applications. The Al PCM should be encapsulated in either a quartz or ceramic capsule.

4.4 Conclusions for Al-Stainless Steel EPCM Performance

There is great interest in using metal PCM for high temperature TES because of the decreased charging/discharging times resulting from the higher thermal conductivity of metals over that of solid salts. From the latent heat of fusion and heat capacities of Al, 79% of the total thermal energy stored for a 100 degree temperature bracket centered on the 660°C melting point of Al is from latent heat storage. This high percentage of latent heat storage would reduce the mass of Al needed to store the same amount of energy for a 100 degree temperature difference than with sensible heat storage alone.

From the results presented in this chapter, it was concluded that Al can be used as a metal PCM for use in high temperature TES at temperatures up to 720°C. The results of the short-term calorimetry testing for the Al-stainless steel EPCM samples were all within the ±2% accuracy of the calorimeter system. Thus, the sample did not experience a loss of storage capacity during these approximately 5 hour short-term thermal cycles.

However, after the Al-stainless steel EPCM samples were exposed to high temperatures for 500 hours there was a 4.1% decrease in storage capacity. Additionally, there was a 10.4% decrease in storage capacity after the Al-stainless steel EPCM was exposed to high temperatures for 1,000 hours. This loss of storage capacity was caused by a reaction between the Al PCM and stainless steel capsule. Therefore, it is concluded that while Al is a good choice of a metal PCM that has many advantages over using a salt PCM, it also has its own disadvantages of being more reactive with metal capsules. Therefore it should be encapsulated in either a non-reactive metal or quartz or ceramic capsule.

CHAPTER 5

SUMMARY & CONCLUSIONS

5.1 Summary

With the recent realization over the past several decades that the fossil fuel resources the world so heavily relies on are truly limited, research into an efficient renewable energy has intensified. One area where research is being focused on is that of using solar energy. The drawback of solar energy, however, is the lack of an efficient way to store solar energy during times of poor solar radiation as to not disrupt the power production of the solar power plant. The most promising form of energy storage for use at solar power plants it that of TES. In order to decrease the volume of material required to store the large amounts of energy required by a solar power plant, one can utilize the latent heat of phase change. As an example for the two PCMs studied here, for a 100 degree temperature swing center on the melting point of the PCM, the percentage of energy stored that is from latent heat storage was 80% for NaCl and 79% for Al. However, difficulties can arise during the heat transfer process due to the low thermal conductivity of most PCM currently used. To alleviate this issue, the PCM can be encapsulated in order to increase the heat transfer area and thus reducing the total heat transfer time. Additionally, to use TES at CSP plants operating Brayton cycle gas turbines, research into high temperature PCMs that can be used for TES is needed.

To study the performance of candidate high temperature PCMs, an immersion calorimeter was specially designed and built. The designed calorimeter system consisted of an insulated container of 4.5kg of silicone oil. The effective heat capacity of the calorimeter system was obtained through calibration. The overall accuracy of the system was determined to be within ±2%. The accuracy of the system not only lends confidence to the calorimeter's ability to measure the thermal energy stored in an EPCM sample but also the experimental method used.

The calorimeter system was used to study the performance of two candidate PCMs, one salt and one metal. Each PCM was encapsulated in 2.54cm diameter by 5.08cm stainless steel capsules. The storage capacity of each EPCM sample was studied after both short and long-term exposure to high temperatures to determine if a loss of capacity would occur in the sample. To determine the storage capacity of the samples, they were first heated to a preselected temperature and then submerged in the calorimeter. The change in temperature of the calorimeter was then used to calculate the total energy stored in the sample.

The salt PCM that was studied was NaCl and was chosen because of its high melting point of 800°C, pushing the temperature at which thermal energy storage can occur to a new limit. The results of the short-term calorimetry testing on the NaCl-stainless steel EPCM samples were also within the ±2% accuracy of the calorimeter system and the samples did not show a decrease in the storage capacity after repeated cycles. After the short-term cycles were complete the NaCl-stainless steel EPCM samples were exposed to 850°C for 1,000 hours. The samples were tested in the calorimeter after the long-term exposure was complete and the results of these experiments had an average error of -2%, still within the accuracy of the calorimeter system. Therefore it was concluded that the NaCl-stainless steel EPCM samples did not experience any loss of storage capacity after either short or long-term exposure to high temperatures. However, micrographs of the NaCl-stainless steel EPCM taken after all testing was completed indicated the presence of at least some level of reaction between the NaCl PCM and the stainless steel capsule. Therefore while NaCl is a good choice of a salt PCM for use in high temperature TES, it should be encapsulated in a less reactive material, such as a nickel based alloy or quartz, to ensure no loss of storage capacity will occur after prolonged exposure to high temperatures.

There is great interest in using metal PCM for high temperature TES because of the decreased charging/discharging times resulting from the higher thermal conductivity of metals over that of solid salts. However, reactions between the PCM and metal capsules appear likely which was also observed some other metals [28] [29] [30]. The results for the short term calorimetry testing of the Al-stainless steel EPCM samples were well within the ±2% accuracy of the calorimeter. From these results it was concluded that the Al-stainless steel EPCM samples did not show a decrease in storage capacity after repeated short-term cycles. Therefore, Al can be used as a PCM for use in high temperature TES at temperatures up to 720°C. However, after the Al-stainless steel EPCM samples were exposed to high temperatures for 500 hours there was a 4.1% decrease in their storage capacity. There was an additional decrease in storage capacity when the Al-stainless steel EPCM samples were exposed to 720°C temperatures for 1,000 hours resulting in a final decrease in storage capacity of 10.4%. The loss of storage capacity was a result of a reaction between the stainless steel capsule and the Al PCM. While an Al-stainless steel EPCM is not a good PCM capsule combination for high temperature TES, Al is a viable PCM but it should be encapsulated in a less reactive material, such as quarts or ceramics.

5.2 Conclusions

Based on the results of all the calorimetry tested performed on the NaCl-stainless steel and Al-stainless steel EPCM samples, the following conclusions were drawn.

- Al and NaCl both have high percentages of latent heat storage for a 100 degree temperature range centered on the melting point, 79% and 80% respectively
- Both Al and NaCl are a good choice of PCM for high temperature TES
- An Al PCM allows for TES at temperatures up to 720°C, while NaCl can be used at temperatures up to 850°C
- NaCl-stainless steel EPCM samples did not show a reduction in storage capacity after long-term exposure to high temperatures
- Al-stainless steel EPCM samples did show a reduction in storage capacity of 4.1% after 500 hours and 10.4% after 1,000 hours.

Therefore it is recommended that while both Al and NaCl are good choices for PCM in high temperature TES at CPS plants, they should both be encapsulated in either quartz or ceramic capsules to ensure no loss of capacity over the lifetime of the EPCM.

REFERENCES

[1] Energy Information Administration, "Monthly Energy Review March 2012," 2012.

[2] Energy Information Administration, "Levelizd Cost of New Generation Resources in the Annual Energy Outlook," 2011.

[3] S. M. Hasnain, "Review on Sustainable Therma; Energy Storage Technologies, part I: Heat Storage Materials and Techiques," vol. 39, 1998.

[4] Pilkington Solar Internation GmbH, "Survey of Thermal Storage for Parabolic Trough Power Plant," 2000.

[5] U. Herrmann and D. W. Kearney, "Survey of Thermal Energy Storage of Parabolic Trough Power Plants," vol. 124, 2002.

[6] "Phase-Change Thermal Energy Storage, Final Subcontract Report on the Symposium Held October 19-20, 1988, Helendale California, Luz International Ltd, Solar Energy Research Institute, CBY Associates Inc.," 1989.

[7] M. Kenisarin and K. Mahkamov, "Solar Energy Storage Using Phase Change Materials," *Renewable and Sustainable Energy Reviews,* vol. 11, 2007.

[8] M. M. Farid, S. K. Khudhair, S. Razack and Al-Hallaj, "A Review on Phase Change Energy Storage: Materials and Applications," *Energy Conversion and Management,* vol. 45, 2004.

[9] H. Mehling and L. Cabeza, "Phase Change Materials and Their Basic Properties,"

Thermal Energy Storage for Sustainable Energy Consumption, 2007.

[10] G. Lane, "Solar Heat Storage: Latent Heat Material, Volume I, Background and Scientific Principles," 1983.

[11] G. Lane, "Solar Heat Storage: Latent Heat Material, Volume II, Technology," 1986.

[12] B. Zalba, J. Marin, L. Cabeza and H. Mehling, "Review on Thermal Energy Storage with Phase Change: Materials, Heat Transfer Analysis and Applications," *Applied Thermal Engineering,* vol. 23, 2003.

[13] A. Sharma, V. Tyagi, C. Chen and D. Buddhi, "Review on Thermal Energy Storage with Phase Change Materials and Appllications," *Renewable & Sustainable Energy Reviews,* vol. 13, 2009.

[14] Y. Zheng, W. Zhao, J. Sabol, K. Tuzla, S. Neti, A. Oztekin and J. Chen, "Encapsulated Phase Change Materials for Energy Storage - Characterization by Calorimetry," *Solar Energy,* 2012 .

[15] W. Zhao, Y. Zheng, J. Sabol, K. Tuzla, S. Neti, A. Oztekin and J. Chen, "High Temperature Calorimetry and Use of Magnesium Chloride for Thermal Energy Storage," *Renewable Energy,* 2012.

[16] D. Colvin, "Enhanced Thermal Management Using Encapsulated Phase Change Materials An Overview, Advances in Heat and Mass Transfer in Biotechnology," *HTD,* vol. 363, 1999.

[17] J. Blaney, *Thesis: Stresses in Containment Vessels for Encapsulated Phase*

Change Materials, Mechanical Engineering and Mechanics Depatment, Lehigh University, 2012.

[18] J. Blaney, S. Neti, W. Misiolek and A. Oztekin, "Stresses in Containment Capsule for Encapsulated Phase Change Materials," *Applied Thermal Engineering,* 2012.

[19] W. Zhao, S. Neti and A. Oztekin, "Heat Transfer Analysis of Encapsulated Phase Change Materials," *Applied Thermal Engineering,* 2012.

[20] W. Zhao, A. Oztekin, S. Neti, K. Tuzla, W. Misiolek and J. Chen, *Thermal Analysis of Encapsulated Phase Change Materials for Energy Storage, in: ASME-IMECE, Denver, Colorado, USA, November 11-17,* 2011.

[21] W. Zhao, *Dissertation: Thermal Energy Storage Using Encapsulated Phase Change Materials,* Mechanical Enguneerung and Mechanics Department, Lehigh University, 2012.

[22] Y. Zheng, *Dissertation: "In Progress",* Chemical Engineering Department, Lehigh University , May 2013.

[23] F. P. Incropera, D. P. Dewitt, T. L. Bergman and A. S. Lavine, "Appendix A Thermophysical Properties of Matter," in *Fundamentals of Heat and Mass Transfer*, Hoboken, NJ, John Wiley & Sons, Inc., 2007, p. 931.

[24] L. Solomon, W. Zhao, Y. Zheng, J. Sabol, K. Tuzla, S. Neti, A. Oztekin and J. Chen, "Sodium Chloride for Thermal Energy Storage - Encapsulated Phase Change Material," *Applied Thermal Engineering*, 2012 (under review).

[25] G. Janz, C. Allen, N. Bansal, R. Murphy and R. Tomkins, Physical Properties

Data Compilations Relevant to Energy Storage II Molten Salts: Data on Single and Multi-Component Salt Systems, Washington, D.C.: U.S. Department of Commerce, National Bureau of Standards, 1979.

[26] M. Chase, *NIST-Janaf Thermochemical Tables,* National Institute of Standards and Technology, 1998.

[27] R. MacDonald, "Enthalpy, Heat Capacity, and Heat of Fusion of Aluminum from 366.degree. to 1647.degree.K," *Journal of Chemical & Engineering Data*, vol. 12, no. 1, pp. 115-118, 1967.

[28] J. Sabol, *Thesis: Characteriation of Intermediate Phases Formed Between Solid Nickel and Liquid Zinc During Cycling for a Solar Thermal Energy Storage System*, 2012.

[29] J. Sabol, W. Misiolek, A. Oztekin and S. Neti, "Characterization of Intermediate Phases Formed Between Solid Nickel and Liquid Zinc During Use as an Encapsulated Phase Change Material in Solar THermal Energy Storage Systems," *Metallography, Microstructure, and Analysis* , 2012.

[30] W. Zhao, Y. Zheng, J. Sabol, A. Oztekin, S. Neti, K. Tuzla, W. Misiolek and J. Chen, *Thermal Energy Storage using Ainc as Encapsulated Phase Change Material, Proceedings of the ASME 2011 International Mechanical Engineering Congress & Exposition,* Denver CO, 2011.

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