Final Report

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Recipient: Abengoa Solar LLC

Address: 11500 W. 13th Ave.
Lakewood, CO 80215

Award Number: DE-FC36-08GO18156

Awardee: Abengoa Solar LLC

Subcontractors: NREL, University of Wisconsin,
NETZSCH, Sigma-Aldrich, Tranter, Alfa-Laval
Packinox, ORNL

Contacts: Keith Gawlik
Project Manager
Phone: 303-323-9170
Fax: 303-928-8510
Email: keith.gawlik@solar.abengoa.com

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Executive Summary: Thermal energy storage systems using phase change materials were evaluated for trough systems that use oil, steam, and high temperature salts as heat transfer fluids. A variety of eutectic salts and metal alloys were considered as phase change materials in a cascaded arrangement. Literature values of specific heat, latent heat, density, and other thermophysical properties were used in initial analyses. Testing laboratories were contracted to measure properties for candidate materials for comparison to the literature and for updating the models. A TRNSYS model from Phase 1 was further developed for optimizing the system, including a novel control algorithm. A concept for increasing the bulk thermal conductivity of the phase change system was developed using expanded metal sheets. Tranter and Alfa-Laval Packinox were contracted to design and cost systems using platecoil heat exchangers immersed in the phase change material. Laboratory evaluations of the one-dimensional and three-dimensional behavior of expanded metal sheets in a low conductivity medium were used to optimize the amount of thermal conductivity enhancement. ORNL was contracted to perform corrosion testing; however, that work did not begin during this budget period. The thermal energy storage systems were compared to baseline conventional systems. The best phase change system found in this project, which was for the high temperature plant, had a projected cost of \$25.2 per kWh_{th}. The best system also had a cost that was similar to the base case, a direct two-tank molten salt system.

Background: Thermal energy storage using phase change material storage media has been considered an attractive option for concentrated solar power plants for decades [SERI]. Materials of interest have been investigated for various purposes for even longer. NIST [Janz] and Kenisarin [Kenisarin] summarized decades of research into the melt temperatures and enthalpies of fusion of hundreds of salts. Only recently has computational capacity increased to the point where transient computational analysis has become practical and modeling has justified prototype construction. The German Aerospace Center (DLR) has contributed significantly to the literature on PCM storage recently, including papers on modeling and prototype testing of PCM storage systems for direct steam generation plants [Michels, Laing]. Additionally, there has been some research on methods of enhancing the thermal conductivity of salts [Mesalhy].

Introduction: Commercial concentrated solar power (CSP) is more accommodating to energy storage than other solar technologies. Energy can be stored at relatively high efficiencies in the form of thermal energy. Thermal energy storage increases plant capacity factors and improves dispatchability. Reducing the capital cost of TES technologies will also result in a reduced cost of energy and ultimately serve as an enabler for commercial solar power plants.

While the ultimate goal is to demonstrate the TES options with the best cost reduction potential for parabolic troughs, the focus of Phase 2 is to design an optimized thermal energy storage system with greater than 50% EPC cost reduction compared to the baseline two-tank system. This is being done through

the development of a model that integrates the thermal energy storage system with the solar field and power block, the use of cost functions from two heat exchanger manufacturers for the components to be used in the proposed cascaded phase change material (PCM) approach, corrosion testing, experimental determination of phase change material thermo-physical properties, experimental determination of thermal conductivity enhancement methods, and the comparison of the model to experimental results from a benchtop phase change experiment.

The two most promising TES concepts from Phase 1 were carried over to Phase 2 for further evaluation.

Task 9: Component Development

Some TES concept options will require the development of novel heat exchangers, according to their function and particularities of the fluid used. Development of other components may be needed as well. Specific activities include:

- a. Define design criteria
- b. Identify and select heat exchanger suppliers
- c. Develop cost functions
- d. Design heat exchangers for Phase 3
- e. Preliminary design review and cost estimates

Task 10: Integrated Model Development (using CFD and TRNSYS or suitable alternatives)

The model developed in Phase 1 will be improved by comparing the model results to published data, integrating TES into the advanced full plant model, calculating the performance of novel heat exchanger types identified in task 1, evaluating the use of TES in direct steam generation (DSG) systems, and other modifications. Specific activities include:

- a. Integrate PCM with advanced full plant model
- b. Modify code for novel heat exchanger types
- c. Include controls
- d. DSG model and controls
- e. Comparison of model predictions to published data

Task 11: Component Testing

The TES fluids and any thermal conductivity enhancements will need to be evaluated for physical properties and corrosivity of typical heat exchanger materials. Heat transfer coefficients from the literature or an experiment will be reviewed for use in the model. Specific activities include:

- a. Testing of PCM materials for thermo-physical properties
- b. Selection of final PCM compositions

- c. Corrosion testing
- d. Thermo-physical testing of thermal conductivity enhancements
- e. Natural convection data

Task 12: Performance and Economic Analyses

The performance and cost analyses will be updated with performance and cost data

obtained during testing. Specific activities include:

- a. Optimize cascaded system design
- b. Investigate TES for DSG and high temperature heat transfer fluids
- c. Compare baseline and PCM TES plants
- d. Review economic analysis and adjust inputs as necessary
- e. Down-select to the most promising candidate for Phase 3, with emphasis placed on the system that has a topology supportive of higher temperatures (650 to 700°C) in an evolutionary manner.

Project Results and Discussion: The project results are organized according to SOPO tasks, as shown below.

Task 9: Component Development Heat Exchanger Development

During Phase 1 of this research effort, multiple tank/heat exchanger designs were considered. The three categories considered were large shell and tube heat exchangers, small shell and tube heat exchangers, and large tanks with submerged plate and frame heat exchangers. During phase 1, small shell and tube heat exchangers were the focus due to the lack of accurate cost data for the alternatives by our EPC contractor. In Phase 2, this lack of information was remedied by contracting directly with heat exchanger manufacturers.

Originally, two heat exchanger companies were contracted in order to develop both a shell and tube and plate and frame solution in parallel. However, upon review of our application and technology both companies have proposed plate and frame solutions. The comparison of the preliminary cost data shows that this solution offers a tangible cost reduction over shell and tube solutions and, as such, Abengoa is content with two competing plate and frame solutions.

The first system, under development by Tranter Inc., uses mechanically deformed plate heat exchanger elements that are electro-welded to form tube-like flow passages. These plates are connected into banks with a built in header system. The banks are then placed into a large salt tank with a piping distribution system hung from the ceiling. Figure 1a shows a typical Tranter plate design and the bank design currently being used in the Tranter based design. Figure 1b shows the integrated bucket design for Bucket 1 using Tranter technology. Buckets 2 and 3

have nearly identical layouts but utilize larger or smaller tanks and different numbers of heat exchanger banks in order to achieve the correct thermal capacity.

Figure 1a: Typical Tranter heat exchanger plate element and current bank design

Figure 1b: Cold bucket design using Tranter heat exchangers

The current Tranter design has been thoroughly modeled using the TRNSYS modeling approach developed in Phase 1. This development effort has included

significant cooperation between Tranter and Abengoa as neither party possesses the expertise to execute on both the heat exchanger design and modeling. Figure 2 shows the phase change and power performance of the Tranter system on our design day, May 25th.

Figure 2: Phase change and power performance of the current Tranter system

The Alfa-Laval system (Fig. 3) is similar to the Tranter system in that it is composed of plate elements connected into larger banks and arranged in a tank. The plates themselves are quite different. Alfa-Laval makes laser welded hydraulically expanded plate systems. These systems do not have any plate spacing between the tube elements like the Tranter system does. They instead act much more as a wall of continuous tubes.

Figure 3: Current bucket 1 designs using Alfa Laval plates (left) and bank assemblies (right)

The current Alfa Laval systems have also been thoroughly modeled using TRNSYS. The ability to store 6 hours of full load energy on our design day has been verified and, more importantly, the repeatability of charging and discharging

has been validated. Figure 4 shows the power and phase change performance of the Alfa Laval system.

Figure 4: Phase change and power performance of the current Alfa Laval system

Ultimately, the two plate designs have very similar performance. The thermal conductivity of the bulk salt is so much lower than that of the heat exchanger that the overall performance is dominated entirely by the bulk salt. Since the performance is similar, the important difference between the two for this application is the cost.

In order to determine the most optimal system for our application, both groups developed cost functions over a wide range of variables. These will cover different plate materials, path lengths, plate spacing, plate designs, and tank sizes. The cost functions were used to develop optimized systems with accurate costs.

Alfa Laval developed internal cost functions based on many different configurations. The variables used to develop these correlations and the valid ranges are given in Table 1. The correlations developed by Alfa Laval are proprietary to Alfa Laval and as such Abengoa was only given a worksheet that could be used to generate cost estimates based on given inputs.

Table 1: Variables and ranges used in the Alfa Laval cost functions.

	Surface area (m ²)	Plate spacing (mm)	Plate length (m)	Plate width (mm)	# plates per module	Config	Thickness (mm)	HTF Flow rate (kg/s)
Minimum	9000	100	5	800	6	2	0.8	600
Maximum	72420	350	10	2000	16	3	1.5	5500

In order to integrate these results into the model, cost correlations needed to be developed. This would have been a prohibitively complicated task for all the variables used in the Alfa Laval worksheet. To simplify the problem, only the surface area and plate spacing were used. All the other variables were fixed based

on the constraints of the problem. Table 2 shows these constant variables and their values.

Table 2: Constant variables used in model cost correlations

Plate length (m)	Plate width (mm)	Number of plates per module	Config	Thickness (mm)	HTF Flow rate (kg/s)
10	2000	12	2	1	2000

This left the plate spacing and total system surface area as the two remaining independent variables. In order to general a cost correlation based on these values, 42 different combinations were tested and a levelized cost per area was calculated for each combination. This cost per area is used by the model to generate a total system cost. The correlations derived using this method are summarized in Equation 1 and Equation 2. These correlations match the Alfa Laval cost estimation sheet within 0.5% and have been developed for both stainless steel 304 and duplex 2205.

$$HX_{cost,lev,SS304} = 8569.31 - 1406.87 \ln(A_{surf}) - 185.73 \ln(L_{spacing}) + 60.35 \ln(A_{surf})^2 + 4.81 \ln(L_{spacing})^2 + 14.86 \ln(A_{surf})^2 \ln(L_{spacing})^2$$

Equation 1

$$HX_{cost,lev,dup} = 8569.31 - 1406.87 \ln(A_{surf}) - 185.73 \ln(L_{spacing}) + 60.35 \ln(A_{surf})^2 + 4.81 \ln(L_{spacing})^2 + 14.86 \ln(A_{surf})^2 \ln(L_{spacing})^2$$

Equation 2

Task 10: Integrated Model Development (using CFD and TRNSYS or suitable alternatives)

Review of PCM TES Performance Model

The phase change material thermal energy storage (PCM TES) concept performance was analyzed using the TRNSYS model developed for Phase 1 of this project and described in that report. In summary, the analysis used a two-dimensional implicit heat transfer model on an adaptive spatial grid integrated into a TRNSYS component. During each time step, the thermal resistance between nodes is calculated using a backwards Euler scheme and the resulting set of temperatures are calculated using a Gauss-Seidel iterative solver. In between time steps, the node network and temperatures are adjusted to account for phase change. This PCM TES component was integrated into a full transient solar power plant model in TRNSYS.

Updates to TRNSYS Model

During this phase, the TRNSYS model described above and in the Phase 1 report was extended and improved in several ways. The solar field and power block components were rewritten to improve flexibility and accuracy by replacing

correlation-based calculations with detailed physical models. The PCM TES component was extended to allow for operation with steam/water as the heat transfer fluid and to include the heat exchanger geometries developed by the heat exchanger manufacturers.

Solar Field Model

The discretized solar field model was created by breaking a single loop into sections, and modeling each section assuming only one-dimensional radial heat transfer, as discussed extensively in [Forristall]. A schematic of the quasi-steady state heat transfer model implemented by Forristall is shown in Figure 5 below.

Figure 5: Forristall's 1-D Receiver Model, [Forristall].

The discretized solar field model, unlike Forristall's model, neglects the resistance to heat transfer posed by convection from the interior of the receiver tube to the

heat transfer fluid. This was done to reduce computational time and modeling complexity and validation showed that this simplification did not significantly impact results.

This solar field model shows excellent agreement with the model based on published literature heat loss correlations over the range of those correlations and conservation of energy and mass were checked.

Power Block Model

The correlation-based power block model was also replaced with a detailed physical model. The steam cycle was modeled externally using GateCycle, the state of the art steam power cycle modeling tool. A schematic of the cycle is shown in Figure 6.

Figure 6: Diagram of steam cycle as implemented in GateCycle

An on-design model case was created for each desired temperature/pressure/power rating combination and detailed performance tables were created for the design and off-design conditions. This method allowed direct comparisons between plants with different operating conditions and improved the accuracy.

Controller

The goal of this improvement was to adapt the plant control strategy to minimize the CPQ. In phase one, the control strategy from the two tank baseline system was directly adapted for the PCM system. Because the PCM system had different strengths and weaknesses (higher storage density but poorer heat transfer), parts of the old control system were inappropriate and inefficient.

Four major changes to the control strategy were made.

1. The TES system was discharged to maximize power block efficiency. The baseline system always runs at maximum discharge rate but the PCM system can benefit from running at lower mass flow rates but higher temperatures.
2. The power block was run in feedwater heater bypass mode at night to help it discharge to a lower temperature.
3. The leftover energy in the cold bucket just before sunrise was used for startup.
4. Excess charge in the coldest bucket was discharged in the morning to preheat the solar field inlet HTF flow to increase the mass flow rate to the undercharged hottest bucket.

The efficiency predictor is a new piece of code that roughly but quickly models the PCM cascade to predict the outlet temperature for many mass flow rates then calculates the power block efficiency for each set of outlet conditions. The plant is then set to operate at the conditions that produced the highest discharge efficiency. The advantage of this scheme is that the power block efficiency is maximized by operating at the highest possible temperature for a given heat flux. Since the system discharges unevenly (as opposed to the two tank baseline which always discharges at a constant temperature), sometimes the outlet temperature can be increased by decreasing the mass flow rate.

Efficiency Predictor

The efficiency predictor code runs in two sections during each discharge-mode time step in the controller component. In the first iterative call, the outlet temperature is calculated from a simplified physics model. The code calculates an equivalent resistance radially from the HTF through the PCM. This code assumes all the solid PCM is in a ring around the pipe with the liquid further out. The equivalent resistance is converted to a UA which is in turn used in an effectiveness/NTU calculation to determine the energy flow from the PCM to the HTF. The effectiveness is estimated based on the amount of liquid PCM remaining. The code is run 70 times over the range of acceptable mass loads. The power block efficiency matrices are called for each run to find and the maximum efficiency.

The code runs for three time steps at the mass flow rate calculated to maximize efficiency. In the third iterative call to the controller, the outlet temperature calculations are corrected based on the output of the actual PCM cascade code. First, the simplified model is run again at the optimized mass flow rate. A correction factor is calculated from the actual outlet temperature divided by the predicted outlet temperature. The simplified code is run again for twenty mass flow rates in the neighborhood of the previous ideal flow rate. Each of these outlet temperatures is multiplied by the correction factor to improve the estimate then used to find the new maximum efficiency. The code then runs continuously until convergence with the new optimum flow rate.

The simplified model predicts the outlet temperature very well for time steps near the beginning of discharge and the overall model works well at all time steps when the correction factor is added. The average error in the outlet temperature prediction with the correction is 1.5%.

Running the plant at maximum efficiency during discharge caused the greatest reduction in CPQ of all the controller changes as seen. There are three reasons for this. First, converting the stored energy to electricity at a higher efficiency means that more electricity can be produced from the same stored energy. Second, the TES system becomes less limited by low heat transfer rates because it is discharging over a longer total time each night. Third, the system can run at low flow rate to discharge low temperature energy at the end of the night when it would have turned off under the old control strategy. The second and third effects cause the number of time steps spent in that operational mode to double.

Nighttime Feedwater Heater Bypass

In the baseline systems, the steam generator feedwater heaters are bypassed during times of very high insolation to decrease the temperature exiting the power block and returning to the solar field. This is done to avoid dumping energy in the solar field. The second baseline system suffered from a related problem during TES discharge. The coldest bucket rarely fully discharged at night and the leftover energy had to be dumped to the solar field. Therefore, bypass mode was used to increase the temperature difference between the cold bucket and the incoming HTF, increasing the heat transfer, and reducing the amount of energy dumped.

In the mode 3 controller code, the feedwater heater bypass control function was changed to be calculated from the power block inlet heat and the energy dumped from the solar field. When the solar field was dumping energy or power block is producing more work than would be possible not in bypass mode, the controller calculates a new bypass control function. The control function is the sum of the excess heat accepted by the power block and the energy dumped by the solar field normalized by dividing by the maximum extra heat the power block can accept in bypass mode.

In the previous model, the cold and middle buckets only discharged to 1% and 12% solid, respectively, before the power block shut down on the design day (May 25). After this change was instituted, they discharged to 7% and 32% solid respectively as seen Fig. 7. Results were similar on all days.

Figure 7: Comparison of charge/discharge for design day with and without feedwater heater bypass

Dumped energy was reduced by 12% because more energy was discharged from the TES at night. This generated more electricity and increased the effective capacity of the cold bucket for the next day.

Preheating Plant from Cold Bucket

During phase one, the control strategy reset the cold bucket to the fully discharged state by dumping energy through the solar field at night. In this phase, two new uses for that energy were adopted. The first was using the flowing HTF through the cold bucket to the solar field and the power block in the time step just before operation began to warm up the plant.

This strategy allows the plant to start producing energy from the solar field earlier instead of using that energy to heat the plant. During the test period in May, this primarily benefits the storage system because the solar field is producing enough energy to send some to storage at almost every time step, even in the very early morning. During other parts of the year, this change should also increase the production from the solar field.

Hot Bucket Boosting from Cold Bucket

Preheating the plant from the cold bucket did not fully balance the charge across the buckets; the coldest bucket was still overcharged during many time steps. Another possible way to solve this was to increase the mass flow rate to the hot bucket at the expense of the cold bucket. This could be accomplished by discharging the cold bucket into the solar field when the solar field was operating below maximum mass flow rate.

A simple scheme to predict whether there would be enough capacity in the solar field to use this scheme was written. Each day was assigned a “good day” or “bad day” tag based on the integrated hourly insolation over the day. The threshold for a good day was optimized and set to 29 kWh/m². One hundred ten days are above this threshold and more than 20 MWh of solar energy are dumped on each of those days. This very simple predictive scheme was chosen because it is unknown how accurately the weather can be predicted. It is expected that the prediction will at least be good enough to guess if the next day will be

predominately sunny or cloudy. This predictor was added to the code as a module listing the expected integrated insolation for the next day at each time step.

The mode 9 controller code was edited to not discharge the cold bucket through the solar field when it was predicted that this strategy could be used. When the next day's insolation is very high the cold bucket energy is still dumped to the solar field. In the mode 3 controller code, the mass flow rates were reassigned and the inlet temperatures were recalculated to account for the new mass flow rates. The scheme is turned on when the mass flow rate through the solar field is less than 90% of the max flow rate and remains on as long as there is latent heat stored in the coldest bucket and the bypass control function remains less than one. The scheme is not run when the solar field is near capacity to avoid dumping energy.

The mass flow rate inputs and outputs required changes to describe these flow patterns accurately. The old scheme was replaced with a system in which the flow into (from sources other than the preceding bucket) and out of each bucket was specified. Any difference between the inlet and outlet flow carries through to the next bucket in the cascade.

Overall, the structure of the PCM code remained the same. However, in order to accommodate an inlet and outlet between each bucket three new node types were necessary: an internal heat transfer fluid (HTF) node, an external HTF node, and an inlet node. Additionally, the removal of the HTF node from the code was necessary as it is replaced by the new internal and external HTF nodes. The internal HTF node is a direct copy of the original HTF node, but unlike the original, is not used for the first HTF node in each bucket.

The inlet node is a boundary condition node with no mass or thermal properties. It is assigned a single constant temperature for each TRNSYS time step. This node serves as a floating boundary condition inside the solutions space in order to allow the model to solve for the entire system simultaneously.

This change was ineffective for the current system. It almost never turned on. This strategy would certainly improve with a better prediction strategy. If it becomes evident that better prediction will be available, the controller should be changed to use more detailed data to guess if the strategy will be useful.

PCM TES Model

The PCM cascade component was updated to allow for steam/water to be used as the heat transfer fluid. Generally, changing the HTF from oil to water required tracking more HTF properties, accounting for changes in those properties in the energy balance heat transfer equations, and correcting for latent heat changes with a system like the grid adjuster. Similarly to the PCM side, it was assumed that the heat transfer energy balance equations could be solved assuming that all heat fluxes caused changes in sensible energy then, in a second step, the sensible energy changes could be converted to latent energy changes as appropriate. This process is shown in Fig. 8.

Figure 8: Flow chart showing how heat transfer is distributed to sensible and latent energy

The first change was to add variables to track the quality and density in every steam/water node. These were initialized similarly to the other thermal properties before solving iterations began. It was assumed that heat transfer between the steam and water during two phase flow was very high such that no superheating or subcooling occurred during boiling or condensing. This is consistent with the homogeneous flow model used. Because the thermal properties of steam are very different from those of water, the existing thermal properties were divided into two sets, one for steam and one for water. This simplified model was used because calling the steam tables every time the values were needed would be excessively computationally expensive. Saturated mixture properties were calculated treating the fluid as a homogeneous mixture based on the properties of the steam and liquid separately. This method under predicts the heat transfer coefficients when compared with empirical results. It was used for its simplicity and to be conservative in a poorly understood system.

The second change consisted of adding a temperature independent term to the A matrix (which contains the $n+1$ coefficient terms in the heat transfer equation) to account for energy added or lost from a node due to changes in quality. This term

tracks the energy flow into and out of the node based on the latent energy in the form of steam entering and exiting the node. A corresponding value was added to the solution array. Because the Gauss-Seidel method converges best for diagonally dominant matrices, the A matrix values were divided by 10,000 to keep their magnitudes small and the corresponding value of the solution array was set to 10,000 to offset this change.

This method includes some unresolved inaccuracies. The mass flow rate out of a node does not depend on changes of the mass of the node. Since the new quality is calculated in a second step after the heat transfer is calculated, this effect cannot be included in the heat transfer calculations. This causes the flow of latent energy out of the node to be incorrect for time steps when the quality is changing. For example, if the system is discharging the quality of the node will increase causing a decrease in both the mass and density of the node. Therefore, the mass flow rate out of the node will be higher and will carry more latent energy than is accounted for in the node. This inaccuracy can be minimized by using small nodes and small time steps. The overall effect is small as can be seen in the low conservation of energy error.

The third change tracks the changes to the quality, density, and mass after the heat transfer equations are solved. Similarly to the grid adjuster implemented in phase one for the PCM side, each HTF node is checked for a condition in which the temperature has exceeded the saturation temperature but the fluid has not reached a quality of one or the temperature has decreased past the saturation temperature but the fluid has not reached a quality of zero. If either of these conditions occurs, the model converts the excess sensible energy change into a latent energy change, recalculating the quality. The mass inside the node and the density are recalculated based on the new quality. These updated properties are used in the next time step.

At times when the quality of a node changed very rapidly, particularly when the system transitioned from discharging to charging, energy was not conserved well so a fourth change was required. When the mode changes from discharge or standby to charge the code overrides the main solver. Instead, it calculates how long it will take for the incoming fluid to purge the fluid currently in the boiler bucket and the qualities and associated properties are set artificially to values that will be closer to the convergent values. Then, the solver resumes heat transfer at the next time step. Even including the errors due to artificially setting the new quality values, this method reduced the overall conservation of energy error. This method is conservative because the PCM is not charge at all during the brief time while the fluid is changing over.

The PCM TES component was also adjusted to use plate heat exchangers instead of tubes, as was done in Phase 1 (see Task 9 section).

Task 11: Component Testing

PCM Salt testing

The thermophysical properties of PCM materials, specifically salts, need to be quantified for accurate model inputs. While literature searches can provide some of this information, not all of these salts have been extensively studied in the past. Additionally, the literature review frequently has conflicting information for even the most basic properties such as binary and ternary eutectic compositions, the melt point and latent energy. Further information is needed such as the material density as a function of temperature, heat capacitance as a function of temperature, viscosity as a function of temperature and thermal conductivity as a function of temperature.

Due to the inconclusiveness and ambiguity of the literature, it was determined that our best approach for getting accurate information would be to evaluate these materials through third party test laboratories.

Testing labs

Abengoa Solar Inc. lacks the lab facilities or in-house expertise in chemistry to do this sort of testing. It was decided to outsource this work to third party laboratories that provided test services. Abengoa came to working agreements with a number of laboratories: the National Renewable Energy Laboratory (NREL), Sigma-Aldrich, the University of Wisconsin, and NETZSCH.

The testing of salts has been an ongoing and dynamic process. As test data was received we recognized that the literature values were extremely inaccurate in many cases. Modeling and designing low-temperature PCM TES systems for oil troughs with the tested properties showed the systems not to be cost effective.

Due to this, we tested additional materials in a higher operating temperature range in hopes of finding a combination of materials that showed favorable economic thermal energy storage savings. This materials testing will be discussed in a later section.

Low Temperature Salt PCM Thermophysical Properties Testing

NREL

The initial plan was for NREL to test the thermo-physical material properties of low temperature PCM salt candidates for use in cascaded, latent energy storage systems. The low temperature PCM storage system is appropriately suited for the operating temperatures of trough solar fields that use an oil-based heat transfer fluid. NREL had the capabilities to test the salts material properties such as the melt point, latent heat of fusion, and heat capacity as a function of temperature using a Differential Scanning Calorimeter (DSC). However, not all of the materials and material properties of interest were completely evaluated.

The test results and collaboration efforts with NREL under FOA funding were incomplete due to many extenuating circumstances. During the materials testing, the laboratory facility was concurrently being developed and the equipment was being shaken down. Additionally, a robust test protocol had not been established, so in many instances it was unclear how to appropriately handle, preprocess and condition the materials to achieve reliable, repeatable test results.

Despite their inexperience with these materials and the equipment, the lack of a fully outfitted laboratory, plus the redirection of DOE goals for testing salts, some valuable data was collected. A summary plot of NREL's test results can be seen in Fig. 9.

Figure 9: The DSC test results from NREL. These values are close to the literature and we have confidence that these are within 10% of the real properties.

The cost of the salt is divided by the tested latent energy to give specific storage cost in dollars per kilojoule on the y-axis. A comparison can be made to the literature latent values in black. The cost of the salts remained constant when comparing the tested values to the literature. NREL's full report is in Appendix A.

The high temperature PCM salt candidates were not tested with NREL.

NETZSCH

NETZSCH Laboratory is a test equipment vendor with a group that specializes in contract test services. This laboratory was contracted to quantify the onset melt point, latent heat of fusion, and heat capacity as a function of temperature using a DSC.

It was initially desired that NETZSCH test ten salts; however, since Abengoa does not have the laboratory resources to store, handle, and mix these materials a compromise was found. To assist in the formulation of these salts, NREL provided a service under their FOA agreement to prepare and ship the formulated salts to NETZSCH. Since a few of the component salts were not readily available to NREL, only 8 of the 10 desired compositions could be mixed and sent for testing.

Test results using NaNO_3 demonstrated their ability to accurately condition and test these salts. For this particular salt, the results were on par with reliable publications and corroborated NREL's test results. A summary plot of NETZSCH's test results can be seen in Figure 10. Again, the cost per unit latent heat is on the y-axis. A comparison can be made to the literature's latent heat values in black. The cost of the salts remained the same when making any comparisons.

Figure 10: The DSC test results from NETZSCH. These values are close to those tested by NREL and we have confidence that these are within 10% of the real properties.

Additionally, NETZSCH provided the heat capacity measurements as a function of temperature. Using a different standard to calibrate the DSC, the values for specific

heats of the salts were reported in the solid phase and liquid phase of the salts. This measurement was problematic for the more aggressive salts such as the hydroxides (any salt containing the OH⁻ cation) due to the necessity of using of a gold plated crucible. Since these crucibles are significantly higher in mass than the usual crucibles, their use produces relatively low accuracy results due to a significantly damped signal response. This was evident in the testing of KOH where negative values specific heats were reported. Fortunately, these materials are so corrosive and the latent energy is so poor that Abengoa has opted not to consider these for use in an actual system. Therefore the poor results of these tests will not affect this work.

Additional testing was performed by NETZSCH to determine the salt's thermal diffusivity using a Laser Flash Analyzer (LFA). This test in conjunction with the heat capacity measurements and the density measurements taken at the University of Wisconsin can be used to calculate the thermal conductivity of the liquid salts as shown in Equation 3.

$$\alpha(T) = \frac{k(T)}{\rho(T)c_p(T)} \quad \text{Equation 3}$$

Of the eight salts, only six could be analyzed. The two salts containing the hydroxides were too corrosive to be contained in the test crucibles. A summary plot of the conductivity as a function of temperature is shown in Figure 11.

Figure 11: The LFA test results from NETZSCH. The conductivities of the six salts tested are very low regardless if they are a liquid or solid. Also note they are all approximately the same conductivity. This clearly shows the need for enhancing the thermal conductivity of the PCM.

From these results, it was determined that all of the salts tested thus far have a conductivity of less than 0.7 W/mK. Due to the low conductivity of these materials and the need to include TCE in the system design, additional time and money spent on salt conductivity testing for the sake of screening materials was not required.

NETZSCH's full report on DSC and LFA results are in Appendix B.

Sigma-Aldrich

Sigma Aldrich is a chemical supply company with the ability to provide custom formulations of materials and some test services. This laboratory was contracted to mix the 10 salt compositions and use a DSC to quantify the onset melt point, latent heat of fusion and heat capacity as a function of temperature.

Sigma-Aldrich's reported results were incomplete and inaccurate. Their inability to quantify accurately simple single component salts such as NaNO_3 and KOH demonstrated that their methods were not correct. Of the ten salts tested only one

matched the data for latent energy and onset melt temperature reported by our other two laboratories.

The cause of these poor results was due to Sigma deciding to complete these test services long before a purchase order was in place. Since we had not reached agreement yet on payment terms, Sigma-Aldrich refused to share test results with Abengoa prior to the release of the purchase order. Therefore, they worked blindly through the entire process without providing Abengoa any incremental feedback on their test approach or test results.

Months later, when a purchase order was finally approved for their services, Sigma-Aldrich finally shared the withheld test results. These results proved to be unacceptably inaccurate. Additionally, information in their report never provided the requested heat capacity measurements as a function of temperature.

A conference call was held after Abengoa reviewed their report. The call revealed that they had not read our email correspondences explaining the exact scope of work, advice on testing approaches, and the deliverables. After the conference call, Sigma-Aldrich wanted to provide satisfactory results and continue doing testing for Abengoa. They said that they would look into re-evaluating their approach and retesting the materials; however, to this date nothing has been resolved.

Sigma-Aldrich's draft report for their DSC tests is in Appendix C.

University of Wisconsin

University of Wisconsin, Madison has extensive experience in the handling and testing of molten salts with a fully equipped laboratory. The University of Wisconsin procured and formulated all of the salt compositions identical to the formulations tested by the other laboratories.

The role of UW was to test the solid and liquid density for ten salts identified as good candidates for low temperature PCM storage systems. The solid density measurement was tested near room temperature. It was assumed that the density change at the elevated temperatures in the solid phase would not significantly bias our analytical models.

Liquid density was tested at six temperatures above the melt point so that a function with respect to temperature could be drawn through the test points. These results are critical for a few purposes. First, density is required to model natural convection flows of the liquid salt. Secondly, density is needed to calculate the thermal conductivity, k , of the liquid. Density was used in conjunction with NETZSCH Laboratory's thermal diffusivity and heat capacitance measurements in order to calculate thermal conductivity as previously mentioned. Figure 12 shows a summary table of the regressed liquid density functions while Figure 13 shows the summary of solid density tests compared to the literature.

No	Salt or salt mixture (mole fraction, %)	Density ρ : [g/cm ³], T: [°C]
1	NaNO ₃	$\rho = 2.140 - 0.7534 \times 10^{-3} T$
2	(80.00)NaOH-(20.00)NaCl	$\rho = 1.977 - 0.5531 \times 10^{-3} T$
3	(72.34)NaOH-(20.48)NaCl-(7.17)Na ₂ CO ₃	$\rho = 2.014 - 0.4948 \times 10^{-3} T$
4	KNO ₃	$\rho = 2.111 - 0.7320 \times 10^{-3} T$
5	(33.00)NaCl-(23.99)KCl-(43.01)LiCl	$\rho = 1.670 - 0.8576 \times 10^{-3} T$
6	(58.72)LiCl-(41.28)KCl	$\rho = 1.861 - 0.4956 \times 10^{-3} T$
7	KOH	$\rho = 1.787 - 0.1707 \times 10^{-3} T$
8	(9.30)K ₂ CO ₃ -(90.70)KOH	$\rho = 1.962 - 0.5201 \times 10^{-3} T$
9	(50.83)MgCl ₂ -(22.10)KCl-(27.06)NaCl	$\rho = 2.110 - 0.7027 \times 10^{-3} T$
10	(42.89)Li ₂ CO ₃ -(31.31)Na ₂ CO ₃ -(20.34)K ₂ CO ₃ -(5.47)NaNO ₃	$\rho = 2.282 - 0.5232 \times 10^{-3} T$

Figure 12: Liquid density functions of potential PCM candidate salts as a function of temperature.

No	Salt or salt mixture (mole fraction, %)	Theoretically* Density ρ : [g/cm ³]	Measured Density ρ : [g/cm ³]
1	NaNO ₃	2.2570	2.2831
2	(80.00)NaOH-(20.00)NaCl	2.1370	2.0050
3	(72.34)NaOH-(20.48)NaCl-(7.17)Na ₂ CO ₃	2.1664	2.0165
4	KNO ₃	2.1090	2.1265
5	(33.00)NaCl-(23.99)KCl-(43.01)LiCl	2.0799	1.9062
6	(58.72)LiCl-(41.28)KCl	2.0333	1.9200
7	KOH	2.0440	2.0760
8	(9.30)K ₂ CO ₃ -(90.70)KOH	2.0669	2.0494
9	(50.83)MgCl ₂ -(22.10)KCl-(27.06)NaCl	2.2036	2.1199
10	(42.89)Li ₂ CO ₃ -(31.31)Na ₂ CO ₃ -(20.34)K ₂ CO ₃ -(5.47)NaNO ₃	2.2895	2.3491

Figure 13: Solid density of the potential PCM candidate salts.

University of Wisconsin's report on the low temperature PCMs is in Appendix D.

High Temperature Salt PCM Thermophysical Properties Testing

Our next steps were to continue material property testing of salt candidates that could provide a cost effective cascaded thermal energy storage system applicable for high temperature solar fields. This TES configuration may be suitable for a molten salt trough plant that can operate at temperatures of 525° C, or a molten salt tower plant that can operate in excess of this temperature.

The thermophysical properties testing was done primarily through NETZSCH which quantified the latent energy, specific heat, thermal diffusivity, and melt temperature of the PCM candidates using their DSC and LFA. Also in this temperature range a few metal alloys were considered in addition to the salts.

The University of Wisconsin assisted with this second part of the materials testing in two ways. They acted as the purchasing agent for the materials and mixed the

salt formulations. Secondly, they did the density testing of the salts which was information that was used as we down selected the most promising materials.

University of Wisconsin

The University of Wisconsin procured all of the salts and mixed the prescribed compositions that were of interest to Abengoa based on a literature review. For some ternary salts, two slight variations on the formulations were mixed due to inconsistencies between the literature publications and the FactSage database. The University of Wisconsin distributed identical samples to NETZSCH for DSC testing.

The University of Wisconsin also procured custom formulated metal alloys from Milward Alloy, a New York based company. These metals were found in literature reviews and showed potential for use as a PCM due to their promising melt temperatures, published latent energies and their high conductivities.

The role of UW was to test the solid and liquid density for ten salts, four metals and paraffin wax (which has been used extensively by Abengoa Solar in bench top experiments that will be discussed later in this report). The salts and metal alloys (Fig. 14) were identified through literature searches as good candidates for high temperature PCM storage systems. The solid density measurement was tested near room temperature.

	Material Composition	Expected Melt Temp [C]	Expected Latent Heat [kJ/kg]	Source/Comments
1	KCl - MgCl ₂ (69.8 -30.2)	435C	351	FactSage (69.8 -30.2) Kensarian has a few mixtures near this but there are a lot of peritectic points according to the FactSage binary plot.
2	CaCl ₂ – KCl - MgCl ₂ - NaCl (41.6 - 2.2 - 8.8 - 47.4)	460C	245	
3	CaCl ₂ – KCl - NaCl (50 - 7.25 - 42.75)	465C	245	
4	KCl - CaCl ₂ - MgCl ₂ (31 – 22.5 – 46.5)	487C	342	The melt point is questionable.
5	CaCl ₂ - CaF ₂ – NaF (50 – 1.5 – 48.5)	490C	264	
6	CaCl ₂ - NaCl (52.1 -47.9)	495C	236	Kensarin (52.8 - 47.2) FactSage (52.1 -47.9)
7	KF - KCl - K ₂ CO ₃ (33 - 44.7 - 22.3)	528C	283	
8	KF - KBr (40 – 60)	576C	315	
9	NaCl - MgCl ₂ (56.9 – 43.1)	430C	320	FactSage (56.9 -43.1) Kensarin (56-44)
10	Li ₂ CO ₃ - Na ₂ CO ₃ - K ₂ CO ₃ (41.3 – 32.6 – 26.1)	394C	273	FactSage
11	Al - Mg - Zn (56.8 - 37.4 – 2.4) (by mass)	443C	310	Metal Alloy
12	Al - Mg (62.9 - 37.1) (by mass)	497C	285	Metal Alloy
13	Al - Si - Cu (68.5 – 5 – 26.5) (by mass)	525C	364	Metal Alloy
14	Al- Si (87.8 – 12.2) (by mass)	557C	498	Metal Alloy (Alloy 413)
15	“Zamak” – Zn-Al-Mg (~96.0 ~ 4.0 ~ 0.05 by mass)	383C		Metal Alloy. Provided by Abengoa
16	Paraffin Candle Wax	52C		Provided by Abengoa

Figure 14: List of high temperature materials of interest. University of Wisconsin procured and formulated these salts and distributed them to our other test laboratories.

Liquid density was tested at six temperatures above the melt point so that a function with respect to temperature could be drawn through the test points. Table 3 shows a summary table of the regressed liquid density functions and the solid density at room temperature.

No.	Mixtures (Mole fraction %)	Liquid Density $\rho: [\text{g}/\text{cm}^3], T: [^\circ\text{C}]$	Solid Density $[\text{g}/\text{cm}^3]$
1	KCl - MgCl_2 (69.8 – 30.2)	$\rho=1.700-1.560 \times 10^{-4}T$	2.1733
2	CaCl_2 - KCl - MgCl_2 - NaCl (41.6 - 2.2 - 8.8 - 47.4)	$\rho=2.079-2.882 \times 10^{-4}T$	2.2932
3	CaCl_2 - KCl - NaCl (50 - 7.25 - 42.75)	$\rho=2.202-4.974 \times 10^{-4}T$	2.1147
4	KCl - CaCl_2 - MgCl_2 (31 – 22.5 – 46.5)	$\rho=2.133-6.338 \times 10^{-4}T$	2.1532
5	CaCl_2 - CaF_2 - NaF (50 – 1.5 – 48.5)	NA	NA
6	CaCl_2 - NaCl (52.1 - 47.9)	$\rho=2.026-3.284 \times 10^{-4}T$	2.0775
7	KF - KCl - K_2CO_3 (33 – 44.7 – 22.3)	$\rho=2.215-5.983 \times 10^{-4}T$	2.3605
8	KF - KBr (40 – 60)	$\rho=3.190-17.40 \times 10^{-4}T$	2.7163
9	NaCl - MgCl_2 (56.9 – 43.1)	$\rho=2.586-16.58 \times 10^{-4}T$	2.1069
10	Li_2CO_3 - Na_2CO_3 - K_2CO_3 (41.3 – 32.6 – 26.1)	$\rho=2.230-5.768 \times 10^{-4}T$	2.2011
11	Al - Mg - Zn (56.8 - 37.4 – 2.4) (by mass)	$\rho=2.332-4.734 \times 10^{-4}T$	2.2589
12	Al - Mg (62.9 - 37.1) (by mass)	$\rho=2.446-6.844 \times 10^{-4}T$	2.2285
13	Al - Si - Cu (68.5 – 5 – 26.5) (by mass)	$\rho=3.531-8.305 \times 10^{-4}T$	3.2517
14	Al- Si (87.8 – 12.2) (by mass)	$\rho=2.671-3.151 \times 10^{-4}T$	2.6628
15	"Zamak" – Zn-Al-Mg (~96.0 ~ 4.0 ~ 0.05) (by mass)	$\rho=6.534-9.024 \times 10^{-4}T$	6.7382
16	Candle Wax	$\rho=0.8131-6.088 \times 10^{-4}T$	0.8905

Table 3 : Summary of correlations of density to temperature. Information for salt No. 5 was unavailable due to issues with the melting process and the corrosion.

In addition to the quantitative density test results, we also gained qualitative experience with the corrosivity and anomalous material behaviors of our high temperature candidates.

The fluoride salts were very difficult to work with as can be seen from the extensive corrosion of the pure nickel crucible in Figure 15. Also, conversations with ORNL, which has extensive experience with these salts, corroborated that the amount of cleaning required to make them compatible with metals is extensive and expensive. Due to these factors, we decided not to DSC test these difficult materials based on the estimation we would not be able to make a cost-effective, commercial PCM TES system.

Figure 15: A pure nickel crucible exposed to the reagent grade fluoride salts was corroded in a matter of hours of testing.

Additionally, we learned that upon the first melt of the solid salt formulation, unless the materials are finely pulverized and thoroughly mixed, the salt does not melt near the eutectic temperature. In fact, if the composition is not prepared correctly, each of the salts will behave as they would individually, melting at their different temperatures which are far in excess of the eutectic composition's melt point. This needs to be investigated more so that the implementation of a commercial installation is approached seamlessly and successfully with the proper preparation of material.

University of Wisconsin's report on the high temperature PCMs is in Appendix E.

NETZSCH

It was initially desired that NETZSCH test ten high temperature salts and four metals; however, due to complications in the material behavior and corrosion issues with some of these salts during the density testing at the University of Wisconsin, a shortened set of salts were prepared and tested.

Since Abengoa does not have the laboratory resources to store, handle or mix these materials, University of Wisconsin was contracted to assist in the formulation of these salts for DSC testing at NETZSCH. We opted to test a select group of salts from the original list that focused on binary and ternary salt compositions containing chlorides or carbonate anions. No fluoride salts were tested. Additionally, since there was conflicting information on the formulations of some of

the salts of interest we decided to mix different compositions containing the same salts so that we might better determine which salts were the eutectic compositions. Also, three metals and the wax were quantified in this testing. The list of high temperature materials tested can be seen in Table 4.

Salt Composition	Expected Melt [C]	Component1 Mol %	Component2 Mol %	Component3 Mol %	DSC/LFA Test	Reference
1 MgCl ₂ - KCl - NaCl	335	34.3	40.7	25.0	Yes/No	FactSage
2 KCl - CaCl ₂ - MgCl ₂	487	31.0	22.5	46.5	Yes/No	Literature
3 KCl - CaCl ₂ - MgCl ₂	415	69.4	2.9	27.7	Yes/No	FactSage
4 CaCl ₂ - NaCl	504	52.0	48.0		Yes/No	Literature & FactSage
5 NaCl - MgCl ₂	460	57.0	43.0		Yes/No	Literature & FactSage
6 Li ₂ CO ₃ - Na ₂ CO ₃ - K ₂ CO ₃	394	41.3	32.6	26.1	Yes/No	FactSage
Other Composition	Expected Melt [C]	Mass %	Mass %	Mass %	DSC/LFA Test	Reference
7 Al - Mg - Zn	443	56.8	37.4	2.4	Yes/Yes	Literature
8 Al - Mg	497	62.9	37.1		Yes/Yes	Literature
9 "Zamak" (Zn-Al-Mg)	383	96	<4	<1	Yes/Yes	Literature
10 Candle Wax	48-65				Yes/Yes	

Table 4: The materials that were selected for thermophysical properties testing at NETZSCH. University of Wisconsin formulated the salts while Milward Alloy formulated the metals.

Using the DSC, NETZSCH quantified the onset melt point, latent heat of fusion, and heat capacity as a function of temperature of all the materials. Since the conductivity of the low temperature salts was between 0.2 and 0.7 W/m-K it was decided that Abengoa would not LFA test the high temperature salts for conductivity values. However, the LFA test in conjunction with the heat capacity measurements and the density measurements taken at the University of Wisconsin were used to quantify the thermal conductivity of the metals and the wax.

Test results from the Li₂CO₃ - Na₂CO₃ - K₂CO₃ formulation demonstrated NETZSCH's ability to measure onset melt temperature and latent energy values that were in line with extensive tests completed at NREL. Since a second laboratory would not be performing redundant property testing, NETZSCH's ability to match NREL's results gave us the confidence that the test results for the remainder of our materials were sufficiently accurate for our simulations. A summary plot of their DSC testing work is in Figure 16.

Figure 16: A comparison of the test results with the available published reference properties for the high temperature PCM candidates.

NETZSCH did a comparison of using the DSC at different heating rates. For the most part, the latent energy and onset melt temperature of the salts were unaffected by heating rate. In the testing of the metals, low ramp rates resulted in latent heat decreasing by 13 to 16%.

An additional anomaly observed at the slow heating rate was a dramatic decomposition of the NaCl-MgCl₂ salt. Due to minor variations in the salt formulation that can slightly skew the formulation between two peritectic points, the system became unstable. This can be seen in Figure 17.

Figure 17: Binary phase diagram of NaCl-MgCl₂. A slightly inaccurate composition could result in a reaction taking place and a shifting of the material chemistry to a point of new equilibrium.

The decomposition was possibly initiated when corrosion products formed in the DSC crucible. A comparison of the DSC test at the high ramp rate (20 K/min) and the low ramp rate (5 K/min) can be seen in Figure 18. Since a PCM TES system is a very slowly changing thermal system, charging over the course of a 6 to 10 hour period, the slow DSC heating rates are representative of a salt being heated in an actual application. Due to this and the observed anomaly, the sensitivity of the salt's stability due to compositional inaccuracy will have to be studied further.

Figure 18: Differences in the salt's stability using different heating rates. The top DSC curves were heating the sample at 20 K/min. In the bottom plot, the same composition sample was heated at 5 K/min.

Corrosion testing

When the low-temperature, PCM storage system costs for oil trough solar fields were modeled using the latent energy results from the DSC testing, we found that sufficient cost reductions could not be achievable. We shifted efforts to

consider different PCM salts in a higher temperature range (up to 500C) in an effort to design a cost effective storage system for molten salt solar fields.

Weekly conference calls occurred to narrow the focus of our corrosion testing. Deviations from the original scope of work and the originally intended temperature range resulted in previously planned testing at ORNL that might not be necessary; specifically, the galvanic coupling corrosion testing of different metals.

With the advice from the corrosion experts at ORNL, reviewing the results of our DSC thermo properties testing and our modeling efforts, we selected four candidate salts to study. Additionally, for each of the salts, we selected two different primary metal coupons for corrosion evaluation and one selection of an alternative grade coupon. Should the corrosion testing of the primary metal candidates exhibit premature failure within the 24 hour or 168 hour evaluation, the corrosion testing was to be restarted with a fresh batch of salt and our alternative metal selection.

The salts selected span a 400-500C temperature range in which two of the salts both melt around 400C. The reason for testing both is that the $\text{MgCl}_2\text{-KCl-NaCl}$ salt has a lower cost per unit of latent energy. However, we expect it to be much more problematic than the others. The risks associated with this salt are that it has a tendency to chemically react in the presence of water, making this salt difficult to store, dry, and handle. Based on our laboratories' experiences with the ternary carbonate salt, $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$, is less corrosive and more stable than the others yet more expensive. Also, we selected two other salts that span the rest of the temperature range; NaCl-MgCl_2 that melts at ~440C and $\text{CaCl}_2\text{-NaCl}$ that melts at ~500C. The benefit of using these salts is that they are a binary composition which should make the accurate formulation of the salt and future testing on this salts sensitivity far easier than a ternary mixture.

A few criteria were considered in the selection of the metals. The first is that it would be a metal that could be used in the manufacturing processes by our heat exchanger company. The second is that it would be a corrosion resistant, cost-effective material. And the last is that it would have the mechanical properties to withstand the salt storage temperatures. Since nickel based alloys and SMO stainless would be too costly and duplex stainless would not be able to maintain mechanical strength at high temperatures, this led us to investigate the 300-series austenitic stainless steels.

Based on a literature review, intergranular stress corrosion cracking and intergranular attack (IGA) of chloride salts on metals are the primary corrosion mechanisms in the presence of water. Chromium is the key alloying element that provides stainless steel with passivation giving it corrosion resistance. However, during heating above 500C and in regions near welds, stainless experiences sensitization where the carbon and chromium alloying content form chromium carbide. As this preferentially leaches from the grain boundaries, these areas are left void of chromium and susceptible to chloride attack. Stainless sensitization can be reduced via a couple of approaches; solution-

quenching (heating to around 1100C and rapidly cooling with water), reducing the carbon alloying content, increase the chromium alloying content or add alloying elements that form carbides more readily than with the chromium.

Since solution-quenching is not a practical option for such large tanks and heat exchangers, the other options for minimizing IGA have been considered in the selection of the metals chosen for this testing. A study at Brookhaven Nation Laboratory showed excellent corrosion resistance to $MgCl_2$ -KCl-NaCl using a 310S stainless steel. This stainless steel has the highest levels of chromium (24.0-26.0%) of all the austenitic 300 series steels. While the carbon content cannot be guaranteed to be as low as an L-grade designation (less than .03%) it cannot exceed 0.08%. We have chosen this as our higher cost but lower risk primary candidate for our most aggressive chloride salts.

Another logical choice for testing low cost stainless steels was grade 321. This is a stabilized steel using 0.3-0.7% titanium to preferentially form titanium carbide at the grain boundaries. It contains a maximum amount of 0.08% carbon and a very high chromium content at 17-19% to ensure good corrosion resistance. This grade has also been selected as another high cost, low risk primary candidate for our most aggressive chloride salts.

In some crude tests performed by NREL to determine DSC crucible compatibility with the salts being tested, they discovered that the carbonate salts are significantly less corrosive than the chlorides. Due to this, NREL was able to successfully test the Li_2CO_3 - Na_2CO_3 - K_2CO_3 salt in a 304 grade stainless steel. This will offer us one of the lowest cost stainless steel solutions for this salt. Additionally, we also tested the 321 grade with this salt as a more conservative alternative should the 304 show signs of significant corrosion.

Lastly, we tested aluminum coupons in our salts to see how well a plain 5052 alloy withstands these environments. Originally, when the corrosion testing work was scoped, we were investigating lower temperature storage systems where aluminum TCE could potentially be used in our system as a highly conductive material that could reduce the amount of heat exchanger surface area while increasing the heat transfer rates through the poorly conducting salts. This posed the need for another material compatibility study with aluminum. In addition, we had found a coating that would put an extremely hard, non-porous, corrosion-resistant and electrically insulating oxide layer on the aluminum surface. This coating is called MicraLox and is similar to an anodizing where a 0.001-0.003 inch layer of aluminum oxide is formed on the surface of the material. In the high temperature range of PCMs, we do not believe that aluminum is a viable option for a conductivity enhancement. However, we will still test the aluminum coupons to see how well they withstand these salt environments with and without the coating. It could be valuable information and a material selected for use in another application. And while aluminum would not be a good material selection for a TCE at these temperatures, an expanded metal TCE can be easily made using a corrosion resistant stainless steel

ORNL performed the screening corrosion tests of four 300-series stainless steels and one aluminum alloy in four industrial grade salt mixtures that appeared promising from literature values of properties and materials compatibility, as described above: MgCl_2 -KCl-NaCl, NaCl- MgCl_2 , CaCl_2 -NaCl, Li_2CO_3 - Na_2CO_3 - K_2CO_3 . The ternary chloride salt proved too aggressive for it to be tested at all. The binary chloride mixtures were extremely aggressive to the aluminum alloy, completely dissolving its coupons before the end of the 370-hour test. 310S stainless steel appears to be the best material for the binary mixture with magnesium with an average corrosion rate of 9.7 mils/year. 316L stainless steel showed high corrosion rates in both binary salts. 321 stainless steel appeared best for the binary salt with calcium with a corrosion rate of 4.6 mils/year. The carbonate salt was the most mild to materials, as expected. Corrosion rates for all materials dropped to less than 4 mils/year by the end of the test, which also suggests a corrosion rate dependent on the consumption of impurities in the salts. ORNL's complete report is in Appendix G.

One-dimensional heat conduction experiments

An experiment was designed to determine the thermal conductivity of a composite material containing a substrate (base material) with thermal conductivity enhancement (TCE) material embedded within. This test simply measured temperatures within the test specimen and electrical power through a resistance heater to ensure 1-dimensional, steady state heat transfer through the composite material has been reached. Via this experiment, relative material performance of the effectiveness for a particular TCE concept was screened and ranked. The results of the experiment were relationships showing the amount of thermal conductivity enhancement as a function of void fraction. These relationships were used in early optimization routines that indicated fairly large void fractions of PCM were sufficient to realize large cost reductions in thermal storage. The complete report of the 1-D experiments is in Appendix F.

Multi-dimensional Fish Tank PCM Experiment

Our in-house testing efforts progressed to the point where a small scale three-dimensional phase change experiment was required to better understand the accuracy of our models, assumptions, and the operation of a physical system. A bench top experiment was designed using safe, low temperature heat transfer fluid (tap water) and a low temperature phase change material (paraffin candle wax) contained within a plastic aquarium. This was a multi-purposed experiment that represented the complexity of the multi-physics phenomenon of a PCM TES system; multi-phased, 3-dimensional, transient heat transfer with phase change.

Purpose

The first purpose of this experiment was to see how the one-dimensional heat conduction enhancements and correlations (void fraction versus bulk conductivity) extended to a three-dimensional system with phase change. This helped us learn how to use or modify the one-dimensional correlations when inputting these parameters into our model.

The second goal was to get a preliminary understanding of the operation of phase change systems through collecting data and watching the freeze-thaw process. With temperature data and visualization through time lapse photography, we were able to witness unforeseen system behaviors which allowed us to better understand potential anomalies in PCM systems. This gave us insights into how to design a prototype PCM tank using salts.

The last objective was to validate our analytical models with a well characterized experiment. With the geometry and fluid properties known we expected to be able to input these parameters into the model and compare the predicted and actual heat transfer rates. This helped identify the model shortcomings and showed where the model assumptions were insufficient.

Design

The fish tank and heat exchangers were designed in a way to represent a small section of a PCM storage system. The fish tank was originally a 30 gallon glass aquarium; however, due to the contraction of the wax during freezing, the plate glass was stressed in the corners of the tank to the point of failure. At that point an identically sized tank made from polycarbonate was custom fabricated with solvent welded edges. This tank was significantly stronger than the glass one and withstood the operating temperatures of the experiment (up to 75°C). The inside dimensions of the tank were 30" x 12" x 21".

The heat exchangers were custom designed for the form factor of the fish tank. The need to exactly replicate of a scaled down version of the actual PCM TES system heat exchanger was not important for a couple of reasons. The first was that our models were developed to be capable of accounting for different heat exchanger geometries and mass. Secondly, a two-dimensional finite element heat transfer analysis showed that variations in the heat exchanger geometry or metal conductivity would have little effect on the heat transfer rate since these factors are negligible resistances compared to those of the PCM. Therefore, we designed and machined in-house a heat exchanger with thirteen internal passes. The geometry is shown in Fig. 19.

Figure 19: Design of the custom flat plate heat exchangers. Two mirrored plates were bolted together to form round, internal, serpentine flow channels.

Three flat plate heat exchangers were made and placed in the tank. The center heat exchanger was the one analyzed. This was the most representative due to the system symmetry. The center of the tank was also guarded from the side heat loss and edge effects that could be biasing the two outside heat exchangers.

The plumbing to each of the three heat exchangers were instrumented with flow meters and differential temperature measurements (two-junction thermopiles). Water was the heat transfer fluid. Energy delivered to or extracted from the wax PCM was easily calculated using handbook data for water properties. A fan coil in the water loop rejected heat during a freeze cycle and a residential hot water tank was used to heat the water for a melt cycle. An additional 11 to 15 temperature measurements were made in the wax to estimate the average bulk solid and liquid temperature and local temperature distribution. Valves were placed in the experiment for isolation, water tempering, flow control and to flip-flop the heat exchanger inlet and outlet ports. This was necessary since a PCM system requires the melt cycle to occur from the top of the tank to the bottom of the tank and vice versa for the freeze cycle. This ensures there is always a liquid surface at the top of the tank for expansion and contraction of the PCM. A picture of the experimental system is in Figure 20.

Figure 20: The insulated fish tank experiment. Note the two hot water tanks on the right, the fan coil heat rejection on the left and the plumbing over the three heat exchangers placed inside the insulated rectangular tank.

When high resolution data was collected for model validation, the experiment was completely insulated with 4 inches of rigid foam board to minimize heat losses. The experiment was run multiple times to determine the repeatability of the system. Once quality data had been collected the system was re-run with web cameras placed at the top and front of the tank so that time lapse photos could be captured. The photos were stitched together to make a movie so that days of operation could be condensed into a movie spanning a few minutes. Via the time lapse movies we observed the system's behavior during the freeze and melt processes.

Different expanded metal arrangements were tested in the fish tank to understand if the simple correlation between void fraction and thermal conductivity enhancement was adequate to describe system behavior. A picture from the top of the fish tank containing expanded metal in the melted, liquid wax is in Figure 21.

Figure 21: Looking into the top of the fish tank experiment. Aluminum expanded metal has been added perpendicular to the heat exchangers for thermal conductivity enhancement.

Method of Comparing the Plain Wax and TCE Wax Systems

Our test metric was based on transient heat transfer methods where a step change in the forcing function produces a transient system response from which a time constant can be determined. In other words, the comparative metric for which a system was quantified was the amount of time in minutes to deliver or extract $2/3$ (1 sigma) of the theoretical maximum amount of energy into or out of the system over the operating temperature difference. The temperature difference was determined from the bulk wax temperature (measured with the immersed thermocouples) and the heat exchanger inlet temperature averaged over the duration of the experiment (which was relatively constant).

With the temperature difference known, the system's capacitance was calculated from our known material masses and properties. The paraffin wax comprised approximately 85% of the system's total heat capacitance and was tested at NREL using a DSC (Fig. 22). NREL measured beginning and final melt and freeze temperatures, latent heat, and specific heat as a function of temperature (Fig. 23). Using these two plots, we estimated the sensible and latent energy for any freeze or melt cycle by integrating over the start and finish temperatures from the appropriate curve.

Figure 22: NREL's DSC test results of the wax. This shows the latent energy, onset and end set temperatures for the melt and freeze of the wax. Note the peak temperature phase shift during the heating and cooling cycle.

Figure 23: NREL's DSC test results for quantifying specific heat as a function of temperature.

Heat losses from the system were estimated from the steady state heat transfer rate into the system once the wax had completely melted and the system had become isothermal. The best fit UA_{loss} term (envelope losses) was assumed to be identical for the freeze cycle since the experiment was not disturbed between the two tests. These

values throughout the test were added (or subtracted) from energy measurements across the heat exchanger to determine how much energy was stored in the wax (versus lost through the envelope). This can be seen in Figure 24 during a melt test of the plain wax.

Figure 24: The energy delivered to the wax PCM during a melt and the estimated and calculated heat losses (top). The bottom plot is the integrated energy from the top plot.

Results

We collected validation quality data and ran visualization studies with numerous scenarios. The amount of expanded metal did not significantly reduce the amount of time to transfer heat into the system during the melting process. However, the addition

of TCE did reduce freeze times. This can be seen in Figure 25 and Figure 26 where the x-axis is a non-dimensional group of the independent variables that describe the TCE.

Figure 25: Time in minutes to add 2/3 of the full amount of energy into the system as a function of a dimensionless group of TCE geometry variables.

Figure 26: Time in minutes to remove 2/3 of the full amount of energy from the system as a function of a dimensionless group of TCE geometry variables. Plain wax is the baseline.

Figure 27 shows photos from visualization runs where differences in behavior can be seen between the plain wax and the thermally-enhanced wax during melting. Figure 28 shows the comparison during freezing.

Figure 27: Melting. Observe in the top view that the aluminum TCE did not appear to behave as an extended heat exchange surface. We expected the wax in contact with the TCE to be melted.

Figure 28: Freezing. Observe in the top and side views that the wax is freezing onto the expanded metal sheets as they conduct heat along the strands toward the cool heat exchanger surface.

While the freeze process could have convection contributing to the heat transfer, the reduction in freeze times appeared to be driven by conduction along the expanded metal strands. The lack of effect of TCE amount on melt times may be due to the relatively high amount of convection that occurred in addition to conduction. Since it was not possible to isolate the modes of heat transfer in this experiment, the testing of this hypothesis will have to wait for a future study. In the meantime, the experimental correlation of phase change times to TCE levels can be used in models.

Task 12: Performance and Economic Analyses

Oil Trough with PCM TES Results

Preliminary results for the oil trough with PCM TES system based on literature property values were excellent. The best system was a 3-bucket system using NaNO_3 , NaCl-KCl-LiCl and $\text{MgCl}_2\text{-KCl-NaCl}$. The system specifications are shown in

Table 5.

Table 5: Optimized oil trough PCM TES specifications

	Bucket 1	Bucket 2	Bucket 3
PCM Type	NaNO ₃	NaCl-KCl-LiCl	MgCl ₂ -KCl-NaCl
Melt Temperature [C]	310	346	375
Enthalpy of Fusion [kJ/kg]	175	281	400
PCM Mass [metric tons]	9,575	5,16	5,339
HX Plate Spacing [m]	0.16	0.125	0.075
TCE Volume Fraction [-]	0.1	0.1	0.1

Using the advanced controller, the transient performance was acceptable as shown in Figure 29. The decrease in power production from storage compared to power production directly from the solar field is due to the large approach temperatures across the heat exchangers and the efficiency maximization control scheme.

Figure 29: Transient performance of oil trough PCM TES system

The cost breakdown is shown in Figure 30.

Figure 30: Cost breakdown of optimized oil trough PCM TES system

This system had a CPQ of 0.34 \$/kWh which is a 71% decrease over the baseline two-tank molten salt system.

Unfortunately, the literature property values on which this model was based were not realistic and the system cannot be built as specified. The $\text{MgCl}_2\text{-KCl-NaCl}$ actually melts above the hot HTF temperature so it is not possible to use it as a PCM in an oil trough. Based on the literature search and subsequent testing, no other PCM candidates are available in the 370-380°C melt temperature range. That makes a PCM TES system infeasible for an oil trough.

Real and hypothetical salt mixtures used in the hot bucket melting outside the 370-380° range do not provide any substantial potential for cost reduction. If the melt temperature is lower than 370°, the steam turbine inlet conditions are too cold to allow efficient power cycle operation and the plant efficiency and production suffer. If the temperature is about 380°, the driving temperature difference between the HTF and the PCM is not large enough to fully charge the hot bucket during the day to allow 6 hours of full-load discharge.

High Temperature Systems

Due to the mismatch in temperature ranges between available PCMs and the oil trough system, PCM TES systems were also evaluated for higher temperature systems.

High Temperature PCM Selection

PCMs with melt temperatures in the range 400 to 600°C were evaluated for potential in a PCM TES system. Seventy five candidates including salts and metals were identified. They were evaluated on the basis of enthalpy of fusion, specific heat, thermal conductivity, cost, corrosivity, and other anticipated problems. An easy-to-calculate metric was developed as a first test of these candidates, seen in Equations 4 to 6. The

costs were taken from vender quotes as available and estimated from small quantity prices available from the Sigma-Aldrich catalog otherwise. Enthalpy of fusion, specific heat, and thermal conductivity were taken from literature sources. Corrosion was estimated from previous testing results. Low scores indicate better candidates.

$$Score = \frac{Cost}{H_f + c_p * \Delta T} * ConductivityPenalty * CorrosionPenalty \quad \text{Equation 4}$$

$$ConductivityPenalty = \begin{cases} 1.5 & \text{if } k < 1 \frac{W}{m-K} \\ 1 & \text{else} \end{cases} \quad \text{Equation 5}$$

$$CorrosionPenalty = \begin{cases} 1.1 & \text{if known to be corrosive} \\ 1 & \text{else} \end{cases} \quad \text{Equation 6}$$

Fourteen PCM candidates were selected for further analysis based on low scores on the simple metric and melt temperatures that met system needs. The results are summarized in Figure 31. These PCMs were submitted for property testing.

Figure 31: Preliminary PCM candidate analysis results

Integrated Models

Two high temperature systems were chosen for detailed analysis, in addition to an oil trough plant. The plant designs are summarized in

Table 6.

Table 6: Summary of plant designs

System	Operating Temperature Range	Typical Power Block Efficiency	Bucket types
Oil trough	300-400 °C	36%	3 sensibly heating HTF
Direct steam generation (superheated)	250-450 °C	38%	1 boiling/condensing HTF 2 superheating HTF
Molten salt trough	300-500 °C	40%	~4 sensibly heating HTF

The first was a superheated direct steam generation trough plant, shown in Figure 32. This work was conducted in the spring of 2011. The system design contained one bucket responsible for condensing and boiling the heat transfer steam/water (during charge and discharge, respectively) and two superheating buckets. This model required improvements to the PCM component code to model phase change heat transfer fluids with varying density. PCM storage is an inherently good fit for DSG because the phase changes in the two materials can be set up to coincide for, ideally, well controlled heat transfer.

Figure 32: Plant schematic of superheated DSG

The second is a molten salt trough operating near the range 300 to 500 °C, shown in Figure 33. This overlaps with Abengoa's other DOE project, Development of Molten-Salt Heat Transfer Fluid Technology for Parabolic Trough Solar Power Plants (DE-FC-08GO18038). A TRNSYS model of this plant had already been designed for this system so the only change required was the addition of the PCM TES component. This system should perform very similarly to an oil system with a cascade of buckets heating and cooling the heat transfer fluid (molten salt in this case) in a stepped cascade. The potential benefits of this system are energy density improvements which would lower

capital cost expenditures. The baseline cost for this system is direct two-tank molten salt storage.

Figure 33: Plant schematic of molten salt trough

Direct Steam Generation Results

The direct steam generation (DSG) with PCM TES analysis was completed based on literature property values before the tested values were available. For the basic superheated DSG system, the plant was operated at 100 bar and between 250 and 450°C. Several salt combinations were tried and the optimal combination was NaNO_3 for the boiler/condenser bucket, and NaCl-KCl-LiCl and $\text{MgCl}_2\text{-KCl-NaCl}$. Neither this system, nor any salt combination, showed any cost reduction potential over an oil trough with two-tank molten salt storage. This was largely due to the high cost and poor transient performance of the DSG plant and the high cost and low storage density of the NaNO_3 which dominated the TES system (84% of the total salt inventory). Few PCM's melt in the range applicable for a boiler bucket and those that do tend to have at least two of the negative factors of high cost, low latent heat, and high corrosivity.

It was found that the transient performance of the superheat buckets was hard to control. Good heat transfer performance on the steam side was only possible with velocities near the limit before vibrations and erosion become destructive (~25 m/s). Since the flow rates are variable this is not always possible and the velocity is frequently lower. A typical daily velocity profile and solidification profile for the 3 bucket system is shown in Figure 34.

Figure 34: Velocity and percent solid for superheated DSG for a typical day.

Further penalizing this concept, these analyses were all carried out assuming that the heat exchanger costs were based on the heat exchanger designs described above. However, those plate designs cannot withstand pressures of 100 bar. To build and test a DSG system, another heat exchanger design would be required which would almost certainly be much more expensive.

Molten Salt Trough with PCM TES Results

Due to the encouraging results from the molten salt trough project suggesting that this technology would soon replace oil troughs, an effort was made to optimize a system using molten salt as the field heat transfer fluid with indirect PCM storage. The baseline system was a molten salt salt trough using solar salt and six hours of direct storage. This system had a CPQ of \$0.42/kWhe, based on a TES system cost of \$78.84M and an annual net power production from storage of 180.3 GWh. The cost breakdown is shown in Figure 35.

Figure 35: Direct storage TES cost breakdown [Millions of Dollars]

Eight PCM TES salt combinations were optimized to find the one most competitive with molten salt direct storage. These combinations are summarized in Table 7.

Table 7: Summary of PCM combinations (based on literature properties)

Salt	Melt Temp	H _f	A	B	C	D	E	F	G	H	I
KNO ₃	335	100	x	x	x	x	x				x
Li ₂ CO ₃ - Na ₂ CO ₃ - K ₂ CO ₃	394	273	x					x		x	
MgCl ₂ - KCl - NaCl	380	193			x	x					x
NaCl - MgCl ₂	430	320		x	x	x					
KCl - CaCl ₂ - MgCl ₂	487	342		x	x	x			x	x	
CaCl ₂ - NaCl	495	236	x								
KF - KCl - K ₂ CO ₃	528	283				x					
MgCl ₂ - KCl - NaCl	335	193					x	x	x	x	
KCl - CaCl ₂ - MgCl ₂	415	342					x		x		
NaCl - MgCl ₂	460	320					x	x	x	x	x
CaCl ₂ - NaCl	504	236					x	x			x
Optimized CPQ*			.68	.33	.31	.42	.37	.38	.32	.31	.43

*Based primarily on property values taken from literature. Not realistic with actual salt properties.

For combination H, the system with the lowest optimized CPQ, the total annual production from storage was 162.0 GWh and the total TES cost was \$50.8M. This cost is broken down in Figure 36. The simple cost of storage (storage system cost divided by the thermal storage capacity) was \$25.2/kWh_{th}.

Figure 36: Optimized PCM storage cost breakdown [Millions of US Dollars]

Comment [DAA2]: Not sure of the units

These promising preliminary results were ultimately misleading, however, because the literature data on which they were based was highly inaccurate. After testing the salts' melting points, enthalpies of fusion, and many other properties, none of the low-CPQ systems are feasible. For example, the $\text{MgCl}_2\text{-KCl-NaCl}$ salt's eutectic point is not near 335°C so all systems including that salt are invalid.

After property testing, combination I was considered the most promising. Those four salts' test results showed reasonable agreement with the values reported in Table 7. Unfortunately, that system did not have a CPQ lower than the baseline molten salt system.

Despite the poor reliability of the existing thermophysical property data, several conclusions can be made from this set of models. First, salts containing MgCl_2 tend to have excellent properties for PCM TES applications relative to other salts and very low cost. It is expected that while the properties of individual mixtures may change, this trend will continue. It can be seen from the table that these salts are critical to achieving a low-CPQ system. Unfortunately, these salts have also proven among the hardest salts to test due to their deliquescence and the extremely corrosive nature of the resulting mixture. Therefore, finding a way to test these salts without extreme corrosion and finding their actual thermophysical properties is of primary importance for this future PCM TES study.

Second, the CPQ is driven primarily by three main factors: whether the melt points are spaced appropriately to allow good performance, the hot bucket, and any buckets that have a low latent-heat-to-cost ratio. Very large gaps in the temperature cascade, particularly including the coldest bucket, tend to degrade the performance too much to achieve a low CPQ. The hot bucket needs to have good properties and be designed well because the plates need to be spaced much more closely than the other buckets to achieve high charge and discharge rates at lower temperature differentials. Because

the cost and latent heat can vary by an order of magnitude, one bad salt can drive the CPQ of the whole system.

Conclusions: All tasks were completed with the exception of the corrosion work and final optimization based on compatible materials found in the corrosion study. PCM TES systems were designed and costed for plants using oil, steam, and molten salt as heat transfer fluids and compared to conventional thermal energy storage systems. The best PCM TES system had a cost-to-performance quotient comparable to the base case, and cost-to-stored-energy ratio of \$25.2 per kWh_{th}.

Budget and Schedule: The Phase 2 budget period went from 9-1-2010 to 8-31-2012. The budget for Phase 2 was \$1,507,308, as shown in the PMC123.1 spreadsheet from 4-29-2011. During this period, DOE spent \$1,171,148 and ASI spent \$328,746, for a total of \$1,499,894, 0.5% lower than the budgeted amount. Contracted work occurred later than scheduled due to prolonged payment terms negotiations. The ORNL work did not start during the Phase 2 period but will take place in the final quarter of 2012.

Path Forward: Due to the approximately equivalent cost-to-performance quotient of the PCM TES system for a molten salt plant and the base case, continuation into Phase 3, where prototyping occurs, is not recommended. Valuable information on material properties and TCE performance, and a novel method of controlling a cascaded TES system were developed in the course of this project. The laboratory test results for PCM candidates and the TCE performance characteristics from the wax experiments at ASI would be useful contributions to the literature, and appropriate journals and conferences will be found where this information can be published.

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Appendix A – NREL DSC Report (Final version)

Cascaded PCMs for Thermal Storage Applications

Final Report for Abengoa Solar, Inc

Judith C. Gomez, PhD

Thermal Storage Group

National Renewable Energy Laboratory

Objectives

The focus of this work was the characterization of the thermal and chemical properties of candidate materials for latent heat TES. Candidate Phase Change Materials (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, such as 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.

Approach

The identification of some of the candidate PCMs was performed by a thermochemical evaluation using different sources: Phase Diagrams for Ceramists [1], the NIST Phase Diagrams Database [2], FactSage thermochemistry software [3], and the open literature [4-8]. Discrepancies were found not only with the chemical compositions but also with the eutectic and other invariant reaction temperatures [9].

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 400°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 ultra high purity (UHP) nitrogen gas to be weighed in a balance with a resolution of 0.0001g, and combined at a specific ratio. Mixing was performed in a ceramic container. This container 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.

It was found that for extremely hygroscopic materials, the mixing procedure should be performed inside the glove box under UHP nitrogen gas. The mixing should be performed using mortar and pestle for at least 30 min to have a homogenous mixture.

Heat capacities, latent heats, transformation temperatures and thermal stability of the PCMs were evaluated using a Differential Scanning Calorimeter (DSC) Mettler-Toledo DSC-1 Star^c System and Thermogravimetric Analyzer with DSC (TGA/DSC) Mettler-Toledo TGA/DSC-1 Star^c System. The heating and cooling rates used were 15K/min. 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). These tests were primarily to protect the instruments and 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. Results of these short-term corrosion studies should not be used as a basis for material selection in field applications.

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 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.

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.

Sample	Molten Salt System, wt. %	Reported values		Source
		T_m , °C	ΔH_m , J/g	
0	KNO ₃	335.32	97.25	-
6A1	92.81KNO ₃ -7.18KCl	308	-	[1]
6A2	97KNO ₃ -3KCl	~315	-	[1]
6A3	95.5KNO ₃ -4.5KCl	320	74	[4]
6B	90.72KNO ₃ -9.28KBr	328	-	[1]
6C1	89.98KNO ₃ -2.95KCl-7.06KBr	320	-	[1]
6C2	80.69KNO ₃ -7.44KCl-11.87KBr	342	140	[5]
1A	7.87NaCl-50.88KCl-41.25LiCl	344	-	[1]
1B	34.81NaCl-32.29KCl-32.90LiCl	346	281	[5]
1C	9.491NaCl-48.43KCl-42.08LiCl	350	-	[1]
3B	60.00MgCl ₂ -20.4KCl-19.60NaCl	380	400	[4]
5	34.13Na ₂ CO ₃ -35.69K ₂ CO ₃ -30.18Li ₂ CO ₃	390	-	[1]

5A	5NaNO ₃ - 95PCM5 (see line above)	-	-	-
5A2	10NaNO ₃ - 90PCM5	-	-	-
5A3	15NaNO ₃ - 85PCM5	-	-	-
5B	5KNO ₃ - 95PCM5	-	-	-
5AB1	5KNO ₃ - 95PCM5A	-	-	-
5AB2	10KNO ₃ - 90PCM5A	-	-	-
5AB3	15KNO ₃ - 85PCM5A	-	-	-
5C	5LiNO ₃ - 95PCM5	-	-	-
5AC1	5LiNO ₃ - 95PCM5A	-	-	-
5AC2	10LiNO ₃ - 90PCM5A	-	-	-
5AC3	15LiNO ₃ - 95PCM5A	-	-	-
KOH	KOH	360 or 400	-	[1,4]

Results and Analysis

The corrosion test made it clear that all the crucible materials were stable in the nitrate and carbonate formulations because they did not show any chemical attack from those molten salt systems. 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%). Potassium hydroxide was extremely corrosive to all the metal alloys tested. It did not attack aluminum oxide during the testing period of about two hours. Some pictures are shown in Appendices A.a and A.b.

DSC tests for the nitrate and carbonate systems 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 formulation were tested.

Predominately Nitrate Systems

The averages of the results for the KNO₃-KCl-KBr systems are shown in Table 2. Some DSC plots for this system are shown in Appendices B.a and B.b.

Table 2: Melting and solidification thermal properties of KNO₃-KCl-KBr systems. (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)

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

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. 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 (formulations 6A2 and 6A3). 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.

Formulation 6A3 (95.5wt%KNO₃-4.5wt%KCl) is 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 [4]. 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.

Heat capacity (C_p) was measured for the KNO₃-KCl-KBr systems because these PCMs are thermally and chemically stable under the test conditions. The C_p 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 KNO_3 -4.5wt%KCl has high solid and liquid heat capacities compared with the other PCMs evaluated in the KNO_3 -KCl-KBr system. The heat capacities of pure KNO_3 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 KNO_3 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 KNO_3 .

The viscosity of the samples KNO_3 -3wt%KCl and KNO_3 -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 KNO_3 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 KNO_3 -KCl-KBr system. The solid heat capacities are the lines with a positive slope while the liquid heat capacities are the constant values. The gaps in the data are where the heat capacity spikes to infinity during phase change around 320°C.

Chloride Systems

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 challenges 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 during the evaluation time. The NaCl-KCl-LiCl system was also tested in the DSC because it was less aggressive and more stable than MgCl₂-KCl-NaCl. Some TGA/DSC plots are shown in Appendices C.a and C.b.

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 TGA sensor has less resolution than the DSC sensor. The latter has 120 thermocouples to control and measure the temperatures that are related to the heat flow measurement. The TGA sensor has only one thermocouple. Because of this difference, we believe that the measured values using the DSC are more reliable.

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).

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

DSC results from the NaCl-KCl-LiCl system (samples 1B in 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 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.

Carbonate-Nitrate Systems

The carbonate-nitrate systems were evaluated for the 380°C PCM. In contrast to the chlorides, they were chemically stable with all the crucible materials tested. DSC averaged results for the Na₂CO₃-K₂CO₃-Li₂CO₃-NaNO₃-KNO₃-LiNO₃ systems are shown in Table 4. The eutectic composition PCM5 (34.13 wt.% Na₂CO₃ - 35.69 wt.% K₂CO₃ - 30.18 wt.% Li₂CO₃) reported an invariant melting point at 394°C with a heat of fusion of 272J/g. By adding small amounts of another molten salt like sodium, potassium and lithium nitrates it was expected to decrease the melting temperature. Different combinations were evaluated keeping the eutectic mixture of PCM5 and adding different amounts of NaNO₃, KNO₃, LiNO₃. Some DSC plots for this system is shown in Appendices B.c. and B.d.

Table 4: Melting and solidification thermal properties of Na₂CO₃-K₂CO₃-Li₂CO₃-NaNO₃-KNO₃-LiNO₃ 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)

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	
5	394.16	-	-	272.34	385.11	-	-	228.18	9.05
5A	384.71	398.58	13.87	239.45	394.17	377.66	16.51	226.48	4.80
5A2	385.11	418.05	32.94	216.90	409.88	384.82	25.06	221.42	8.17
5A3	389.02	431.06	42.04	215.52	432.16	383.49	48.67	207.91	0.02
5B	387.61	-	-	246.36	383.41	-	-	221.04	4.20
5AB1	383.41	-	-	233.24	377.85	-	-	235.00	5.56
5AB2	387.34	-	-	224.53	385.24	-	-	209.41	2.10

5AB3	384.67	399.80	15.13	206.86	381.00	-	-	203.83	18.80
5C	385.95	397.38	11.43	253.12	385.52	380.59	4.93	238.03	11.86
5AC1	383.28	423.24	39.96	247.09	403.62	393.41	10.21	234.56	29.83
5AC2	387.23	437.43	50.20	178.18	386.55	430.40	43.85	186.65	50.88
5AC3	385.40	NR	> 50	NR	NR	385.54	> 44	NR	NR

NR: non recorded

The minimum melting point obtained in this system, for a composition with narrow melting temperature range, was obtained for PCM5AB1 (5 wt.% KNO_3 – 4.75 wt.% NaNO_3 – 30.80 wt.% Na_2CO_3 – 32.21 wt.% K_2CO_3 – 27.24 wt.% Li_2CO_3). This formulation shown a melting point at 383°C with a heat of fusion of 233 J/g. The second lowest melting point was obtained for composition PCM5A (5 wt.% NaNO_3 – 32.42 wt.% Na_2CO_3 – 33.91 wt.% K_2CO_3 – 28.67 wt.% Li_2CO_3). Its melting temperature was 385°C with a heat of fusion of 239 J/g. This composition is the best one of the two. It is less complicated than the former one because it has one less component and the values of melting point and heat of fusion are too close.

Previous tests with potassium hydroxide showed that it is extremely corrosive with stainless steel and porcelain due to the silica-based enamel. Its characterization was performed in the TGA/DSC and DSC using alumina crucibles which were completely inert to this salt. Before testing, the salt was pretreated for water removal. It was heated at 300 °C during 30 and 60 minutes and then heated up to 480 °C and 500 °C respectively for melting. The solidification was also resolved during cooling of the molten sample up to 50 °C (TGA/DSC plots are shown in Appendices C.c.i and C.c.ii). The solidification process was resolved in the TGA/DSC as well as in the DSC. The average of four samples showed the beginning of solidification (end of melting) at 398 °C and the end of solidification (beginning of melting) at 359 °C with a heat of solidification/melting of 123 J/g. A solid-solid transformation was resolved during cooling at 246 °C with a latent heat of 70 J/g.

Conclusions and Recommendations

Based on the results, the best molten salt candidate for a 320°C PCM was the KNO_3 -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 KNO_3 -4.5wt%KCl with those of pure KNO_3 (melting point of 335°C), the binary salt has a lower heat of fusion and the liquid heat capacity. Corrosion issues would be greater with the chloride-containing salt. These detrimental effects must be weighed against the more favorable melting point.

The chloride 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 systems. The carbonate system evaluated for the 380°C target has potential as a PCM because it is noncorrosive to aluminum and stainless steel and exhibits heats of fusion over 200 J/g, which are good for a PCM. At this point the only problem is that the lowest melting point obtained of 385°C for formulation 5 wt.% NaNO_3 – 32.42 wt.% Na_2CO_3 – 33.91 wt.% K_2CO_3 – 28.67 wt.% Li_2CO_3 is high for the 380°C target. According to Abengoa's system modeling, the melting point must be lower than 380°C to have a good efficiency at the storage system. Studies are still ongoing to reduce the melting point of this carbonate system.

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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Appendices

A. Chemical Stability (corrosion) Test

- a. MgCl_2 , KCl , NaCl (Bucket 380°C). Performed at 500°C for one hour.

- b. NaCl , KCl , LiCl (Bucket 350°C). Performed at 500°C for 3.5 hours.

B. Differential Scanning Calorimeter (DSC)

- a. $89.98\text{KNO}_3\text{-}2.95\text{KCl-}7.06\text{KBr}$ (PCM6C1) from 230°C to 380°C at 15°C/min using aluminum crucibles.

- b. $\text{KNO}_3\text{-}4.5\text{wt.\%KCl}$ (PCM6A3) from 230°C to 430°C at 15°C/min using aluminum crucibles.

- c. Eutectic $34.13\text{Na}_2\text{CO}_3\text{-}35.69\text{K}_2\text{CO}_3\text{-}30.18\text{Li}_2\text{CO}_3$ (PCM 5) from 300°C to 450°C at 15°C/min using aluminum crucibles.

d. PCM 5 with 5wt.% NaNO₃ from 300°C to 450°C at 15°C/min using aluminum crucibles.

C. Thermogravimetric Analysis with DSC (TGA/DSC)

- NaCl - KCl - LiCl formulation from 120°C to 450°C at ±10°C/min using aluminum oxide crucibles. Mass was lost during the first heating cycle.

- b. MgCl_2 -KCl-NaCl formulation from 120°C to 450°C at $\pm 10^\circ\text{C}/\text{min}$ using aluminum oxide crucibles. Three heating/cooling cycles. First cycle shows an endothermic peak that disappeared during the third cycle.

- c. KOH at $\pm 15^\circ\text{C}/\text{min}$ using aluminum oxide crucibles.
i. Water removal at 300 °C during 30 min. Heating up to 480 °C. Solidification is resolved.

ii. Water removal at 300 °C during 60 min. Heating up to 500 °C. Solidification is resolved.

Appendix B – NETZSCH DSC and LFA Report (Final version)

Applications Laboratory Thermoanalytical Section

**DSC and Specific Heat Capacity Studies of Pure Salts and
Salt Mixtures**

Report Number 621002378

Prepared for:

**Abengoa Solar
11500 West 13th Avenue
Denver, CO 80215**

Work Performed Under Purchase Order Number 45100128686

Submitted By: Beta

Iir A. Beta

Applications Laboratory Scientist

December 2011

NETZSCH Instruments North America LLC, 37 North Avenue, Burlington, MA 01803
Phone 781-272-5353, Fax 781-272-5225, NIB-Sales@netzsh.com

Introduction

The Thermophysical Property Section of the NETZSCH Instruments Testing Laboratory, Burlington, MA, received eight salt samples from Abengoa Solar for measurement of specific heat and melting enthalpies by DSC.

The specific heat was measured using a NETZSCH model DSC 204 F1 differential scanning calorimeter capable of operation from -180 to 700 °C. The system is vacuum-tight, and therefore samples can be tested under pure inert, reducing or oxidizing atmospheres, as well as under vacuum. The specific heat is determined by first running a baseline with empty crucibles and a sapphire standard over the temperature range of interest. The sample is then run and the specific heat is calculated by the standard ratio method. The ratio method for calculating the specific heat capacity is similar to ASTM E1269. Instrument control and data acquisition are accomplished via a 32-Bit MS[®]-Windows[™] Proteus[®] software and electronics system. Data evaluation is carried out by a comprehensive PC software package allowing computation of peak and onset temperatures, inflection points, partial area integration, specific heat, transformation energetics, etc. The DSC 204 F1 can be operated in accordance with national and international standards such as ASTM C351, D3417, D3418, D3895, D4565, E793, E794 and E1269 as well as DIN 51004, -51007, -53765, -65467, DIN EN 728, JIS R 1672 and ISO 10837, -11357, -11409.

Test Parameters

Temperature program	Isothermal at 30 °C for 10 minutes, heat 30 °C to 460 °C at 20 K/min
Purge Gas	Argon, 40 mL/min
Sensor	DSC type E

Crucible	Aluminum, crimped for pierced lids for 6 samples. Gold-plated steel for the KOH and KOH-K ₂ CO ₃ samples
Sample mass	<p>NaNO₃: m = 23.37 mg (1st heating), m = 23.30 mg (2nd and 3rd heating)</p> <p>KNO₃: m = 23.84 mg (1st, 2nd and 3rd heating)</p> <p>MgCl₂-KCl-NaCl: m = 7.95 mg (1st heating), m = 6.77 mg (2nd and 3rd heating)</p> <p>KCl-LiCl (A): m = 7.56 mg (1st heating), m = 7.11 mg (2nd and 3rd heating)</p> <p>NaCl-KCl-LiCl (B): m = 7.78 mg (1st heating), m = 7.17 mg (2nd, 3rd and 4th heating)</p> <p>Na₂CO₃-K₂CO₃-Li₂CO₃-NaNO₃: m = 5.97 mg (1st heating), m = 5.83 mg (2nd and 3rd heating)</p> <p>KOH: m = 9.80 mg (1st heating), m = 7.96 mg (2nd and 3rd heating)</p> <p>KOH-K₂CO₃ (B): m = 12.59 mg (1st heating), m = 10.84 mg (2nd and 3rd heating)</p>

Test Results and Discussion

The DSC specific heat capacity curves for all the samples were calculated using sapphire as standard. A sapphire disk with diameter of 5.2 mm and thickness of 0.25

mm was measured before the sample run using the same baseline and the same parameters (heating rate, purge gas flow rate) as for all the sample runs. A calibration with melting standards (In, Bi and CsCl) was used to obtain more accurate values for the melting enthalpies. In order to create a sensitivity calibration curve, the areas under the melting peaks are calculated in units of $\mu\text{V}\cdot\text{s}/\text{mg}$ and then the conversion factors are calculated based on accepted literature values for the melting enthalpies of the standards in J/g. The calculated conversion factors are then curve-fitted to obtain a sensitivity curve in $\mu\text{V}/\text{mW}$ vs. temperature which is applied to the raw thermocouple signal to get a DSC curve with units of mW/mg. Integration of the peaks in the DSC curve with the sensitivity calibration yields peak areas with energy units of J/g.

The samples were transferred in the DSC pan in air and weighed carefully on an analytical balance with accuracy of 0.01 mg. After the first heating cycle, the DSC pan with the sample was removed from the DSC at a temperature of 150°C, weighed and returned quickly to the argon-purged DSC chamber. The mass after the first heating, which was generally lower than the original mass due to the removal of water, was used for all the subsequent heating cycles.

a) Sample NaNO_3

The DSC specific heat curves for the three heatings of the NaNO_3 sample are plotted in Figure 1. C_p values at 10 °C intervals are given in Table 1.

Figure 1 – DSC specific heat curves for three heatings of the NaNO₃ sample

Table 2 – C_p values for three heatings of the NaNO₃ sample

Temperature [°C]	C _p 1 st heating [J / (g•K)]	C _p 2 nd heating [J / (g•K)]	C _p 3 rd heating [J / (g•K)]
50.0	0.893	0.761	0.649
60.0	0.911	0.776	0.649
70.0	0.923	0.788	0.656
80.0	0.936	0.800	0.667

90.0	0.953	0.817	0.683
100.0	0.970	0.835	0.700
110.0	0.990	0.857	0.720
120.0	1.010	0.880	0.743
130.0	1.033	0.905	0.766
140.0	1.056	0.930	0.791
150.0	1.081	0.958	0.818
160.0	1.109	0.989	0.848
170.0	1.138	1.021	0.880
180.0	1.170	1.057	0.915
190.0	1.206	1.096	0.957
200.0	1.247	1.140	1.003
210.0	1.295	1.192	1.056
220.0	1.351	1.254	1.120
230.0	1.421	1.329	1.201
240.0	1.516	1.428	1.306
250.0	1.638	1.567	1.451
260.0	1.823	1.777	1.675
270.0	2.141	2.167	2.097
280.0	2.861	2.587	2.643
290.0	1.511	1.331	1.360
300.0	1.478	1.281	1.316
310.0	4.297	4.264	4.278
320.0	15.165	14.575	13.912

330.0	1.798	1.917	1.902
340.0	1.337	1.299	1.275
350.0	1.328	1.286	1.258
360.0	1.327	1.283	1.255

The DSC curves with the melting standards calibration are plotted in Figure 2 for three heatings of the sample NaNO_3 . A heating rate of 10 K/min was used for the 3rd heating to investigate the influence of the heating rate. The fact that DSC curve obtained with 10 K/min show much lower signal than the 20 K/min curves is due to the almost linear dependence between the DSC signal and the heating rate. The onset shifts to lower temperatures by 0.5°C when using 10 K/min instead of 20 K/min, while the peak area (melting enthalpy) is almost unaffected.

Figure 2 – DSC curves for three heatings of the NaNO₃ sample

b) Sample KNO₃

The DSC specific heat curves for the three heatings of the KNO₃ sample are plotted in Figure 3. C_p values at 10 °C intervals are given in Table 2.

Figure 3 – DSC specific heat curves for three heatings of the KNO₃ sample

Table 2 – C_p values for three heatings of the KNO_3 sample

Temperature [°C]	C_p 1 st heating [J / (g•K)]	C_p 2 nd heating [J / (g•K)]	C_p 3 rd heating [J / (g•K)]
50.0	0.929	0.743	0.548
60.0	0.947	0.743	0.556
70.0	0.962	0.716	0.530
80.0	0.977	0.668	0.444
90.0	0.989	0.595	0.423
100.0	1.007	0.656	0.464
110.0	1.027	0.816	0.572
120.0	1.045	0.843	0.779
130.0	1.064	0.864	0.903
140.0	4.374	5.837	5.251
150.0	2.572	1.196	1.268
160.0	1.187	1.079	1.184
170.0	1.120	1.080	1.191
180.0	1.114	1.078	1.193
190.0	1.124	1.085	1.207
200.0	1.129	1.088	1.217
210.0	1.136	1.095	1.230
220.0	1.144	1.105	1.238

230.0	1.152	1.116	1.250
240.0	1.161	1.129	1.262
250.0	1.170	1.141	1.274
260.0	1.180	1.156	1.289
270.0	1.189	1.169	1.302
280.0	1.199	1.184	1.316
290.0	1.210	1.200	1.331
300.0	1.222	1.215	1.346
310.0	1.234	1.230	1.360
320.0	1.248	1.243	1.376
330.0	1.273	1.253	1.399
340.0	7.098	6.519	7.331
350.0	3.438	3.754	3.546
360.0	1.299	1.222	1.383
370.0	1.270	1.192	1.360
380.0	1.271	1.191	1.361
390.0	1.274	1.192	1.363

The DSC curves with the melting standards calibration are plotted in Figure 4 for three heatings of the sample KNO_3 . The onset is very stable, especially for the 2nd and 3rd heatings, whereas the melting enthalpy (peak area) varies by about 5%.

Figure 4 – DSC curves for three heatings of the KNO₃ sample

c) Sample MgCl₂-KCl-NaCl

The DSC specific heat curves for the three heatings of the $\text{MgCl}_2\text{-KCl-NaCl}$ sample are plotted in Figure 5. 1st heating shows the desorption of water as two peaks at 238.3°C and 298.8°C. Based on the observation that these peaks are missing in the DSC specific heat curves for the subsequent heating cycles, we can conclude that no desorption of water takes places for the 2nd and the 3rd heating. C_p values at 10 °C intervals are given in Table 3.

Figure 5 – DSC specific heat curves for three heatings of the $\text{MgCl}_2\text{-KCl-NaCl}$ sample

Table 3 – C_p values for three heatings of the $MgCl_2$ -KCl-NaCl sample

Temperature [°C]	C_p 1 st heating [J / (g•K)]	C_p 2 nd heating [J / (g•K)]	C_p 3 rd heating [J / (g•K)]
50.0	1.019	0.871	0.830
60.0	0.991	0.849	0.786
70.0	0.982	0.834	0.772
80.0	0.987	0.815	0.762
90.0	0.993	0.812	0.758
100.0	0.947	0.804	0.762
110.0	0.959	0.788	0.749
120.0	1.013	0.781	0.754
130.0	1.039	0.786	0.754
140.0	1.079	0.781	0.767
150.0	1.130	0.777	0.766
160.0	1.214	0.766	0.756
170.0	1.326	0.754	0.763

180.0	1.498	0.758	0.763
190.0	1.804	0.756	0.764
200.0	2.312	0.780	0.777
210.0	3.118	0.788	0.779
220.0	4.419	0.785	0.782
230.0	6.523	0.785	0.792
240.0	7.875	0.788	0.800
250.0	3.081	0.798	0.816
260.0	2.185	0.802	0.812
270.0	3.093	0.792	0.814
280.0	3.716	0.799	0.816
290.0	3.984	0.797	0.814
300.0	4.836	0.804	0.814
310.0	3.542	0.803	0.818
320.0	2.347	0.812	0.830
330.0	1.804	0.820	0.837
340.0	1.085	0.828	0.846
350.0	0.645	0.847	0.856
360.0	0.632	0.858	0.866
370.0	0.663	0.860	0.879
380.0	0.882	0.965	0.898
390.0	7.710	19.858	19.531
400.0	8.384	13.423	10.765
410.0	6.323	2.124	2.791

420.0	1.689	1.648	1.162
430.0	1.957	1.618	1.129
440.0	2.480	1.293	1.114

The DSC curves with the melting standards calibration are plotted in Figure 6 for three heatings of the sample $\text{MgCl}_2\text{-KCl-NaCl}$. The onset and the melting enthalpy are stable, especially for the 2nd and 3rd heatings. However, the melting peak shape shows large variations between the three heating cycles, possibly because this is not a eutectic mixture. Sample creeping on the crucible walls in irrepeatable manner could also be a contributing factor.

Figure 6 – DSC curves for three heatings of the MgCl_2 -KCl-NaCl sample

d) Sample KCl-LiCl (A)

The DSC specific heat curves for the three heatings of the KCl-LiCl (A) sample are plotted in Figure 7. 1st heating shows the desorption of water as two peaks at 105.1°C and 147.2°C. No desorption of water was detected for the 2nd and the 3rd heating. C_p values at 10 °C intervals are given in Table 4.

Figure 7 – DSC specific heat curves for three heatings of the KCl-LiCl (A) sample

Table 4 – C_p values for three heatings of the KCl-LiCl (A) sample

Temperature [°C]	C_p 1 st heating [J / (g•K)]	C_p 2 nd heating [J / (g•K)]	C_p 3 rd heating [J / (g•K)]
50.0	1.109	0.903	0.836

60.0	1.134	0.883	0.851
70.0	1.192	0.854	0.831
80.0	1.288	0.835	0.819
90.0	1.453	0.823	0.809
100.0	1.864	0.810	0.805
110.0	2.845	0.803	0.799
120.0	2.307	0.790	0.801
130.0	2.760	0.787	0.796
140.0	3.367	0.779	0.796
150.0	3.653	0.771	0.796
160.0	1.198	0.775	0.791
170.0	1.012	0.769	0.795
180.0	0.946	0.765	0.790
190.0	0.931	0.764	0.788
200.0	0.917	0.771	0.792
210.0	0.894	0.776	0.789
220.0	0.886	0.776	0.787
230.0	0.889	0.780	0.784
240.0	0.891	0.795	0.792
250.0	0.896	0.797	0.797
260.0	0.902	0.805	0.801
270.0	0.902	0.818	0.807
280.0	0.899	0.820	0.811
290.0	0.899	0.827	0.814

300.0	0.897	0.840	0.822
310.0	0.894	0.851	0.828
320.0	0.889	0.862	0.833
330.0	0.884	0.892	0.837
340.0	0.884	0.906	0.856
350.0	0.904	0.933	0.866
360.0	15.407	16.329	16.697
370.0	7.231	8.923	6.316
380.0	1.295	1.229	1.159
390.0	1.191	1.138	1.087
400.0	1.178	1.124	1.073
410.0	1.140	1.106	1.064
420.0	1.117	1.093	1.049

The DSC curves with the melting standards calibration are plotted in Figure 8 for three heatings of the sample KCl-LiCl (A). The onset is very stable, whereas the melting enthalpy changes by just over 1% for the 2nd and 3rd heatings.

Figure 8 – DSC curves for three heatings of the KCl-LiCl (A) sample

e) Sample NaCl-KCl-LiCl (B)

The DSC specific heat curves for the four heatings of the NaCl-KCl-LiCl (B) sample are plotted in Figure 9. 1st heating shows the desorption of water as two peaks at 105.1°C and 165.8°C. No desorption of water was detected for the 2nd, 3rd and the 4th heating. C_p values at 10 °C intervals are given in Table 5. The different C_p values after melting are due to creeping effects. When the molten salt creeps up the crucible walls it loses contact with the bottom of the crucible yielding a

smaller DSC signal and as a result a smaller C_p . As a rule, the higher C_p value should be used because that indicates a better contact between the sample and the bottom of the crucible.

Figure 9 – DSC specific heat curves for four heatings of the NaCl-KCl-LiCl (B) sample

Table 5 – C_p values for four heatings of the NaCl-KCl-LiCl (B) sample

Temperature [°C]	C_p 1 st heating [J / (g•K)]	C_p 2 nd heating [J / (g•K)]	C_p 3 rd heating [J / (g•K)]	C_p 4 th heating [J / (g•K)]
50.0	1.027	1.814	1.953	1.990
60.0	1.073	1.856	1.938	2.040
70.0	1.158	1.883	1.941	2.053
80.0	1.296	1.891	1.951	2.065
90.0	1.268	1.892	1.956	2.070
100.0	2.918	1.889	1.958	2.072
110.0	2.865	1.882	1.956	2.066
120.0	2.016	1.874	1.956	2.057
130.0	2.394	1.863	1.955	2.050
140.0	2.928	1.851	1.951	2.043
150.0	3.654	1.819	1.946	2.035
160.0	4.599	1.781	1.941	2.028
170.0	3.288	1.744	1.935	2.016
180.0	1.081	1.712	1.927	2.009
190.0	0.946	1.680	1.921	2.005
200.0	0.987	1.653	1.913	2.000
210.0	0.857	1.635	1.914	2.000

220.0	0.859	1.624	1.916	2.002
230.0	0.789	1.620	1.911	2.010
240.0	0.796	1.599	1.885	2.018
250.0	0.822	1.575	1.870	2.031
260.0	0.854	1.554	1.857	2.050
270.0	0.892	1.536	1.848	2.068
280.0	0.937	1.516	1.845	2.089
290.0	0.982	1.495	1.843	2.114
300.0	1.028	1.475	1.844	2.144
310.0	1.070	1.449	1.855	2.173
320.0	1.111	1.409	1.860	2.190
330.0	1.152	1.380	1.867	2.205
340.0	1.193	1.361	1.882	2.227
350.0	1.351	1.398	1.963	2.298
360.0	10.259	19.838	23.080	24.019
370.0	4.313	3.261	3.529	3.706
380.0	1.688	2.016	2.528	2.822
390.0	1.473	2.031	2.514	2.805
400.0	1.472	2.072	2.537	2.830
410.0	1.518	2.098	2.561	2.877
420.0	1.562	2.153	2.625	2.930

The DSC curves with the melting standards calibration are plotted in Figure 10 for four heatings of the sample NaCl-KCl-LiCl (B). There is some variation in the onset temperature and the

melting enthalpy, possibly due to the sample creeping up the crucible walls. This effect reduces the amount of sample in contact with the bottom of the DSC crucible and is likely to be non-reproducible for the different heating cycles.

Figure 10 – DSC curves for four heatings of the NaCl-KCl-LiCl (B) sample

f) Sample $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{-NaNO}_3$

The DSC specific heat curves for the four heatings of the $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{-NaNO}_3$ sample are plotted in Figure 11. 1st heating shows the desorption of water as two peaks at 94.4°C and 214.2°C. No desorption of water was detected for the 2nd, 3rd and the 4th heating. C_p values at 10 °C intervals are given in Table 6.

Figure 11 – DSC specific heat curves for four heatings of the $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{-NaNO}_3$ sample

Table 6 – C_p values for four heatings of the $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{-NaNO}_3$ sample

Temperature [°C]	C_p 1 st heating [J / (g•K)]	C_p 2 nd heating [J / (g•K)]	C_p 3 rd heating [J / (g•K)]	C_p 4 th heating [J / (g•K)]
50.0	0.644	0.416	0.407	0.391
60.0	0.641	0.392	0.436	0.424
70.0	0.789	0.379	0.454	0.445
80.0	1.214	0.373	0.468	0.463
90.0	2.244	0.371	0.486	0.480
100.0	1.183	0.375	0.503	0.498
110.0	0.572	0.385	0.523	0.521
120.0	0.555	0.396	0.549	0.579
130.0	0.575	0.446	0.633	0.597
140.0	0.640	0.468	0.577	0.568
150.0	0.606	0.424	0.581	0.580

160.0	0.592	0.430	0.597	0.600
170.0	0.609	0.438	0.612	0.619
180.0	0.654	0.447	0.630	0.637
190.0	0.754	0.455	0.646	0.656
200.0	0.954	0.462	0.665	0.672
210.0	1.211	0.468	0.677	0.685
220.0	1.166	0.476	0.696	0.703
230.0	0.783	0.485	0.710	0.721
240.0	0.595	0.498	0.727	0.734
250.0	0.620	0.575	0.742	0.749
260.0	0.669	0.542	0.750	0.766
270.0	0.702	0.558	0.759	0.784
280.0	0.702	0.569	0.770	0.810
290.0	0.683	0.586	0.786	0.829
300.0	0.731	0.611	0.818	0.863
310.0	0.798	0.718	1.022	1.267
320.0	1.751	1.205	0.957	0.918
330.0	0.726	0.495	0.899	0.927
340.0	0.748	0.470	0.935	0.971
350.0	0.799	0.457	0.999	1.035
360.0	0.871	0.308	1.148	0.741
370.0	1.025	0.438	1.325	0.861
380.0	1.043	1.154	2.447	1.700
390.0	2.513	6.575	24.579	10.888

400.0	16.419	10.505	3.498	5.650
410.0	1.503	1.541	1.620	1.590
420.0	1.147	1.107	1.220	1.167
430.0	1.152	1.020	1.148	1.105
440.0	1.166	1.013	1.145	1.102

The DSC curves with the melting standards calibration are plotted in Figure 10 for four heatings of the sample $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{-NaNO}_3$. The peak position and the peak shape vary between the different heating cycles, possibly because the sample is not a eutectic mixture.

Figure 12 – DSC curves for four heatings of the $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{-NaNO}_3$ sample

g) Sample KOH

The DSC specific heat curves for the three heatings of the KOH sample are plotted in Figure 13. Due to its corrosive nature, the KOH sample was measured in a gold-plated steel crucible to avoid any reactions with the crucible material and protect the DSC sensor from potential contamination. However, the use of the heavy gold-plated steel crucibles has the disadvantage that the portion of the DSC signal coming from the sample is small and, hence, one would expect larger errors in the specific heat values. 1st heating shows the desorption of water as three peaks at 111.8°C, 145.2°C and 274.1°C. Very small amounts of desorbed water were detected for the 2nd and 3rd heating as a peak at 107.7 °C. C_p values at 10 °C intervals are given in Table 7.

Temperature [°C]	C _p 1 st heating [J / (g•K)]	C _p 2 nd heating [J / (g•K)]	C _p 3 rd heating [J / (g•K)]
50.0	1.018	1.463	1.483
60.0	1.061	1.429	1.426
70.0	1.158	1.395	1.405
80.0	1.209	1.402	1.405
90.0	1.223	1.419	1.409
100.0	1.237	1.407	1.402
110.0	8.343	2.192	1.662
120.0	6.424	1.663	1.565
130.0	5.317	1.602	1.546
140.0	6.988	1.555	1.545
150.0	5.761	1.570	1.535
160.0	3.124	1.611	1.559
170.0	2.791	1.651	1.585
180.0	2.972	1.695	1.614
190.0	3.354	1.737	1.659
200.0	3.792	1.796	1.700
210.0	4.306	1.863	1.732
220.0	4.849	1.911	1.691
230.0	5.385	1.873	1.684
240.0	5.941	1.842	1.703
250.0	6.375	1.866	1.733
260.0	6.699	6.105	5.898

270.0	6.859	2.351	2.142
280.0	6.833	1.633	1.514
290.0	6.586	1.475	1.417
300.0	6.306	1.450	1.393
310.0	5.989	1.433	1.373
320.0	5.710	1.427	1.360
330.0	5.379	1.412	1.341
340.0	3.783	1.376	1.321
350.0	3.165	1.308	1.289
360.0	2.791	1.328	1.313
370.0	2.493	2.323	2.351
380.0	2.466	1.645	1.813
390.0	2.803	2.006	2.269
400.0	3.691	4.023	4.380
410.0	2.009	9.593	9.892
420.0	1.093	1.885	2.220
430.0	0.802	0.996	1.379
440.0	0.753	0.868	1.277
450.0	0.832	0.849	1.247

The DSC curve with the melting standards calibration for three heatings of the KOH sample are plotted in Figure 14. The standards employed for the DSC calibration consisted of RbNO_3 , KClO_4 and Ag_2SO_4 . The DSC curves for the 2nd and 3rd heating cycle show a sharp peak at 254.0 °C

and 254.1 °C with onset temperature of 251.6 °C and integrated areas of 94.72 J/g and 91.94 J/g. At high temperatures the 2nd and 3rd heating cycles show a double peak feature with peaks at 366.8 °C, 407.9 °C and 366.6 °C, 407.8 °C, onset temperatures of 364.8 °C and 364.6 °C and total integrated areas of 149.7 J/g and 156.3 J/g.

Figure 14 – DSC curves for three heatings of the KOH sample

h) Sample KOH-K₂CO₃ (B)

The DSC specific heat curves for the three heatings of the KOH-K₂CO₃ (B) sample are plotted in Figure 15. This sample was again measured in a gold-plated steel crucible due to its corrosive

properties. 1st heating shows the desorption of water as three peaks at 113.9°C, 133.9°C and 287.9°C. Very small amounts of desorbed water were detected for the 2nd and 3rd heating. C_p values at 10 °C intervals are given in Table 8. Some negative C_p values, especially after the melting, are mostly due to the larger errors in the determination of specific heat when using the heavy gold-plated steel crucibles, but also because of possible reactions between the corrosive salt and the crucible material.

Figure 15 – DSC specific heat curves for three heatings of the KOH-K₂CO₃ (B) sample

Table 8 – C_p values for three heatings of the KOH- K_2CO_3 (B) sample

Temperature [°C]	C_p 1 st heating [J / (g•K)]	C_p 2 nd heating [J / (g•K)]	C_p 3 rd heating [J / (g•K)]
50.0	1.037	1.107	0.682
60.0	1.102	1.007	0.844
70.0	1.133	0.935	1.034
80.0	1.146	0.900	0.805
90.0	1.152	0.891	0.732
100.0	1.179	0.892	0.692
110.0	8.066	1.119	0.912
120.0	7.582	0.990	0.775
130.0	5.728	0.951	0.682
140.0	4.646	0.899	0.650
150.0	2.509	0.891	0.630
160.0	2.129	0.918	0.623
170.0	2.175	0.913	0.618
180.0	2.349	0.910	0.613
190.0	2.606	0.908	0.618
200.0	2.904	0.900	0.597
210.0	3.249	0.880	0.578
220.0	3.632	0.860	0.548
230.0	4.045	0.851	0.529

240.0	4.505	0.840	0.506
250.0	4.928	0.850	0.644
260.0	5.287	4.224	3.431
270.0	5.520	1.076	0.687
280.0	5.666	0.555	0.212
290.0	5.677	0.446	0.096
300.0	5.594	0.380	0.046
310.0	5.396	0.332	0.004
320.0	5.101	0.272	-0.042
330.0	4.781	0.227	-0.090
340.0	4.483	0.270	-0.137
350.0	4.066	0.013	-0.182
360.0	3.833	-0.073	-0.208
370.0	2.938	17.627	18.018
380.0	2.057	3.060	2.917
390.0	1.295	0.037	0.091
400.0	0.672	-0.461	-0.257
410.0	0.137	-0.650	-0.343
420.0	-0.240	-0.829	-0.412
430.0	-0.608	-0.933	-0.463
440.0	-0.835	-0.986	-0.513
450.0	-0.980	-1.017	-0.566
460.0	-1.076	-1.016	-0.602

The DSC curves with the melting standards calibration for three heatings of the KOH-K₂CO₃ (B) sample are plotted in Figure 16. The same calibration was used as for the KOH sample. The DSC curves for the 2nd and 3rd heating cycle show a sharp peak at 254.5°C and 253.8°C with onset temperatures of 251.0°C and 250.8 °C and integrated areas of 69.58 J/g and 68.54 J/g. At high temperatures the 2nd and 3rd heating cycles show another sharp peak at 371.5°C and 371.3°C, onset temperatures of 367.0°C and 366.9°C and total integrated areas of 145.4 J/g and 144.3 J/g.

Figure 16 – DSC curves for three heatings of the KOH-K₂CO₃ (B) sample

Applications Laboratory

Thermophysical Properties Section

Thermal Conductivity of Molten Salt Mixtures

Report Number 621002379

Prepared for:

Abengoa Solar, Inc.

11500 West 13th Street
Denver, CO 80215

Work Performed under PO# 4500128686

Submitted By: _____

Brian Ricks

Applications Laboratory Technician

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NETZSCH Instruments North America, LLC, 129 Middlesex Tpke, Burlington, MA 01803
Phone 781-272-5353, e-mail: nib-sales@netsch.com

Introduction

The Thermophysical Property Section of the NETZSCH Instruments Applications Laboratory, Burlington, MA, received 8 salt samples for thermal diffusivity and specific heat measurements. The specific heat was measured by DSC and the results can be seen in an accompanying report (#621002378). Thermal diffusivity and specific heat values were used to calculate thermal conductivity values for the samples.

The samples identifications are shown below in the results section. They were supplied as powders.

The temperature range for the thermal diffusivity measurements of samples was defined by the melting point as determined from the DSC measurements. Seven temperature points were used between 50°C below the melting point and 70°C above, in 20°C intervals. These measurements were performed by the flash method using a NETZSCH LFA 457 Microflash™ instrument. This instrument and the test method conform to ASTM E1461-01, "Standard Test Method for Thermal Diffusivity by the Flash Method".

Background

Thermal Diffusivity

Transient heat transfer problems occur when the temperature distribution changes with time. The fundamental quantity that enters heat transfer situations not at steady-state is the thermal diffusivity. It is related to the steady-state thermal conductivity through the equation

$$D = \frac{\lambda}{C_{pp}} \quad (1)$$

where

D = thermal diffusivity

λ = thermal conductivity

C_p = specific heat

ρ = density

Thermal properties of materials are measured by experimentally establishing a heat flow boundary value problem, solving the theoretical equations, and then measuring the necessary temperatures or heat fluxes to determine the thermal property by matching to the theoretical solution. Thus, the easiest theoretical way to measure the thermal conductivity is to set up a steady-state, linear flow of heat through the material and apply Fourier's equation. This approach has led to the development of a number of methods for measuring the thermal conductivity including the guarded hot plate and linear rod methods. These methods are time consuming and can be susceptible to errors arising from non-realization of the assumed boundary or steady-state conditions. The flash methods of measuring thermal diffusivity remove the steady-state condition at the expense of measuring temperature as a varying function of time.

The measurement of the thermal diffusivity of a material is usually carried out by rapidly heating one side of a sample and measuring the temperature rise curve on the opposite side, as seen in Figure 1. The time that it takes for the heat to travel through the sample and cause the temperature to rise on the rear face can be used to determine the through-plane diffusivity. The through-plane thermal conductivity can then be calculated if the specific heat and density are known.

Figure 3: Diagram of the flash method for measuring thermal diffusivity

Through-Plane Method

A schematic of the NETZSCH LFA 457 instrument is shown in Figure 2. The sample is normally a disk with a standard diameter of 12.7 or 25.4 mm and a thickness ranging from about 0.1 to 5 mm, although disks and square samples of various sizes can also be accommodated. With the NETZSCH LFA 457 MicroflashTM instrument, the sample disk is aligned in a holder between a neodymium glass laser (1.06 mm wavelength, 330 ms pulse width) and an indium antimonide (InSb) IR detector in a high temperature furnace. A thermocouple near the sample controls the sample and its surroundings at any temperature between 20°C and 1100 °C.

Figure 4: Schematic of the NETZSCH LFA 457

Once the sample has been stabilized at the desired temperature, the laser is fired several times over a span of a few minutes and the necessary data is recorded for each “shot”. The flash energy strikes and is absorbed by the front surface of the sample, causing a heat pulse or temperature wave to travel through the sample thickness. The resulting back surface temperature rise is fairly small, ranging from about 0.5°C to 2°C. This temperature rise is kept in the optimum range by controlling the laser charging voltage and by a filter between the laser and the furnace. The sample back surface is viewed by the IR detector and the temperature rise signal vs. time is amplified and recorded with a high speed A/D converter. An example of a temperature rise curve measured by the IR detector is shown in Figure 3.

Figure 5: Example of a temperature rise curve

The instrument is fully automated to control all systems and record, analyze and report the thermal diffusivity, specific heat and the calculated thermal conductivity.

Samples that do not naturally have a high value of emissivity or absorptivity are coated with a graphite film before testing. The graphite increases the energy absorbed on the flashed side and increases the temperature signal on the back side of the sample. Some materials are transparent to infrared or visible radiation and can be coated with a metal film approximately 1000 Å on both sides. This prevents penetration of the flash energy into the sample on the front side, and on the back side prevents the IR detector from viewing into the sample.

Through-Plane Analysis

In the through-plane measurement depicted in Figure 1, the sample can be thought of as part of a sheet of material infinite in two dimensions but of finite thickness. Before the flash, the temperature of the

sample and surroundings is at some uniform temperature that can be taken as zero. Immediately after the flash, the front surface of the sample is at some higher temperature, T_0 . The heat flux lines are parallel and directed through the sample; there is no heat flow in the plane of the sample. The boundary conditions consist of radiation heat transfer from the front and rear faces into a surrounding space at the initial zero temperature. There have been many solutions of this boundary/initial value heat equation problem in different forms. The first to apply the solution to the flash diffusivity measurement was Parker et al.¹ Using the notation of Koski², the resulting equation for the rear face temperature as a function of time is

$$T(a,t) = 2T_f \sum_{n=1}^{\infty} \frac{\gamma_n^2 (\gamma_n^2 + L^2) \cos \gamma_n}{(\gamma_n^2 - L^2)(\gamma_n^2 + L^2 + 2L)} \exp(-\gamma_n^2 Dt / a^2) \quad (2)$$

where

T_f	=	final adiabatic sample temperature
D	=	thermal diffusivity
t	=	time
a	=	sample thickness
L	=	heat loss factor (Biot number)

Each γ_n is found by solving the transcendental equation

$$\tan \gamma_n = \frac{2\gamma_n L}{\gamma_n^2 - L^2} \quad (3)$$

The finite width of the flash energy pulse, t_p , can affect the measurement of thin and/or high diffusivity samples because the heating of the front surface can no longer be considered instantaneous relative to the time for the heat to diffuse through the sample. To include this effect in the analysis, the pulse width is folded into the results by convoluting Equation (2) with the pulse shape. If there is no heat loss, i.e. $L=0$, and the finite pulse can be ignored, then Equation (2) leads to the Parker expression

$$D = \frac{0.1388a^2}{t_{50}} \quad (4)$$

where t_{50} , the half rise time, is the time for the back face temperature to reach 50% of its maximum value. The constant value of approximately 0.139 is known as the Fourier number. Equation (4) is a very useful expression for calculating optimum sample thickness and expected rise times if the approximate diffusivity is known.

Equation (2) can be used to generate the temperature rise curve if the diffusivity and the loss factor are known. The analysis of the flash data requires the inverse of this operation; the temperature rise curve is known and the diffusivity is to be determined. Depending on the sample and measurement conditions, several different analysis methods can be used¹⁻⁹. The NETZSCH LFA Analysis software has different models which can be selected including combinations of facial and radial heat loss, finite pulse effect, semi-transparent materials, and two and three layer systems^{7,8}. The models are based on non-linear regression routines which take the entire measurement curve (normally 2000 points) into consideration by adjusting the unknown diffusivity and loss factor until the total point by point error between the theoretical and measured temperature rise curves is minimized. The measurement and analysis can then be validated in the software by visual and statistical comparison of the model and measured temperature rise curves.

Specific Heat Capacity

The specific heat capacity (or specific heat) of a material is defined as the amount of energy required to raise a unit mass of material by one unit of temperature at constant pressure,

$$C_p = \frac{Q}{m\Delta T}$$

where:

C_p = specific heat

m = mass

ΔT = change in temperature

Q = energy

Specific heat can be measured with the flash method by comparing the temperature rise of the sample to the temperature rise of a reference sample of known specific heat tested under the same conditions¹. This temperature (voltage) rise is recorded during the diffusivity measurement, so the specific heat can be calculated from the same data with a suitable calibration. Assuming that the flash energy and its coupling to the sample remain essentially unchanged between samples:

$$Q = \text{absorbed energy} = (mC_p\Delta T)_{\text{ref}} = (mC_p\Delta T)_{\text{sample}}$$

and:

$$C_{p\text{sample}} = \frac{(mC_p\Delta T)_{\text{ref}}}{(m\Delta T)_{\text{sample}}} = \frac{(mC_p\Delta V)_{\text{ref}}G_{\text{sample}}}{(m\Delta V)_{\text{sample}}G_{\text{ref}}} \quad (5)$$

A reference sample is measured at each temperature of interest to calibrate the change in output voltage (ΔV) of the IR detector (or thermocouple for low temperature measurements) resulting from the absorbed energy. The measured ΔV divided by the detector amplifier gain (G) will be proportional to the temperature rise (ΔT), as long as the temperature rise is small. This calibration gives the “absorbed energy” or a calibration factor in terms of the mass, specific heat, ΔV and G for the reference sample measurement. When a sample of unknown specific heat is measured, the “absorbed energy” divided by the product of the mass and $\Delta V/G$ of the test sample, Equation 5, gives the test sample specific heat.

The measured ΔV will be affected by heat loss during the measurement, so in order to use ratios of the measured ΔV in Equation 5, the heat loss factor L (see Equation 2) of the reference and test sample should be similar. If the heat loss factors are significantly different, ratios of the theoretical ΔV are used. The theoretical ΔV , or final adiabatic sample temperature T_f , can be calculated from Equation 2 once the diffusivity and loss factor L have been determined as described above.

Testing has shown that the flash energy is stable from pulse to pulse within about $\pm 2\%$, so the average of several pulses at each temperature is used in the calculations. The absorptive efficiency of the front surface of the samples to the flash energy and the radiative efficiency of the back surface to the IR detector are controlled by coating the reference and test samples with the same thin layer of graphite or other suitable coating.

Thermal Conductivity and Thermal Resistance

The sample thermal conductivity can be calculated with Equation (1), with measurements of the diffusivity and specific heat as described above, and with a measurement of the sample bulk density. The bulk density is normally calculated from the measured sample volume (calculated from the measured sample dimensions) and mass.

The thermal resistance is defined as

$$R = \frac{a}{\lambda} \quad (6)$$

where

R = thermal resistance

a = sample or layer thickness

Test Results

Each salt sample was measured using a sample holder designed for liquid metal samples. An argon atmosphere was used for all measurements. The samples were first heated to the highest temperature point, defined as 70°C higher than the melting point determined by DSC. LFA measurements were then performed at each temperature point as the furnace cooled down to the lowest temperature point, defined as 50°C below the melting point determined by DSC. This cycle was then immediately repeated so that two heatings were measured for each complete measurement on each sample.

The specific heat, thermal diffusivity, and thermal conductivity curves for each sample are given in Figures 4, 5, and 6. Additional notes on each measured sample are given on pages 9 to 10.

Many samples required multiple measurements to be performed. The raw LFA data is fitted to a diffusivity model, and several factors can lead to poor fits. In the liquid phase, creeping up the sidewalls of the container can leave a void in the measurement region. A similar void can also be present in the solid phase if the sample does not completely fill the measurement region during cooling and solidification. Measurement runs were rejected if one or both cycles exhibited signs of these voids.

The measurements were first started using an Al-steel container. As multiple measurements were performed with this container, it began to degrade. This degradation negatively impacted the measurement results. A Pt container was obtained and used for the rest of the measurement.

Density data for the samples was provided by Abengoa Solar, however the temperature range of the liquid measurements went beyond the range of provided values. Those values were extrapolated using the linear fits given for the liquid density values.

The specific heat for the samples was measured by DSC. However, because the LFA measurements were performed close to the melting point of the samples, the C_p values were estimated for many of the points. Figures 7 through 12 show the measured DSC- C_p data along with the estimated values.

a) NaNO_3

The NaNO_3 sample was measured once using the Al-steel container. This sample was measured prior to making the change to the wider temperature range. Because the results fit the diffusivity model well and showed no signs of voids, the measurement was not repeated with the wider temperature range. The results for the NaNO_3 measurement are given in Table 1.

b) KNO_3

The KNO_3 sample was first measured twice using the Al-steel container and then repeated once with the Pt container. Neither of the measurements in the Al-steel container were satisfactory. This is possibly due to the Al-steel container beginning to degrade. The results of the KNO_3 measurement with the Pt container are given in Table 2.

c) LiCl-KCl

The LiCl-KCl sample was measured first using the Al-steel container and then repeated twice with the Pt container. The results from the Al-steel container were rejected due to severe degradation of the sample container. The first measurement with the Pt container showed signs sample creep in the liquid phase, so it was repeated. In this repeated measurement, the liquid phase points were acceptable, however the solid phase points were poorly fitted to the diffusivity model. The results of the second measurement with the Pt container are given in Table 3 with the solid phase points omitted.

d) $MgCl_2$ -KCl-NaCl

The $MgCl_2$ -KCl-NaCl sample was measured twice using the Pt container. The first measurement showed large differences between the first and second heat cycles, so it was repeated. The results of the second measurement are given in Table 4.

e) NaCl-KCl-LiCl

The NaCl-KCl-LiCl sample was measured using the Pt container. The results of the measurement are given in Table 5.

f) Na_2CO_3 - K_2CO_3 - Li_2CO_3 - $NaNO_3$

The Na_2CO_3 - K_2CO_3 - Li_2CO_3 - $NaNO_3$ sample was measured using the Pt container. The results of the measurement are given in Table 6.

g) *KOH and KOH-K₂CO₃*

These two samples were tested for compatibility with Pt throughout the temperature range. Both samples melted, blackened, and adhered to the Pt surface. Because similar reactions are also known to happen with aluminum, the Al-steel container could not be used either. Thus, LFA measurements could not be performed for these samples.

Error Propagation

Assumed values of the error for each component of the thermal conductivity calculation are given below. The resulting error in the thermal conductivity is calculated as the square root of the sum of the squares of the component errors.

Density	Specific Heat	Thermal Diffusivity	Thermal Conductivity
±3%	±10%	±5%	±11.6%
±3%	±10%	±10%	±14.5%
±3%	±25%	±5%	±25.7%
±3%	±25%	±10%	±27.1%

A study of the three-layer diffusivity model indicates that the error contributions from the density and the specific heat to the diffusivity calculation are not high enough to amplify any of the above error margins.

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Figure 6

Thermal Conductivity vs. Temperature

Table 1

ASTM E1461 Flash Method Thermal Conductivity Results

Sample	thickness @ 25°C (mm)	bulk density (g/cm ³)	temperature (°C)	specific heat c _p (J/g-K)	diffusivity α (mm ² /s)	conductivity λ (W/m-K)
NaNO ₃ (i) (1st heat cycle)	0.416	1.89	335	1.31	0.223	0.553
		1.90	324	1.29	0.211	0.516
		1.90	314	1.28	0.200	0.485
		1.91	304	1.26	0.182	0.435
		2.28	294	1.25	0.136	0.388
		2.28	284	1.24	0.156	0.441
		2.28	274	1.23	0.144	0.403
NaNO ₃ (ii) (2nd heat cycle)	0.416	1.89	335	1.31	0.197	0.487
		1.90	324	1.29	0.191	0.466
		1.90	314	1.28	0.185	0.447
		1.91	304	1.26	0.179	0.429
		2.28	294	1.25	0.144	0.410
		2.28	284	1.24	0.164	0.463
		2.28	274	1.23	0.150	0.420

Table 2

ASTM E1461 Flash Method Thermal Conductivity Results

Sample	thickness @ 25°C (mm)	bulk density (g/cm ³)	temperature (°C)	specific heat c _p (J/g-K)	diffusivity α (mm ² /s)	conductivity λ (W/m-K)
KNO ₃ (i) (1st heat cycle)	0.595	1.81	405	1.28	0.178	0.412
		1.83	385	1.27	0.175	0.408
		1.84	365	1.27	0.173	0.404
		1.86	345	1.26	0.170	0.399
		1.87	325	1.26	0.167	0.393
		2.13	305	1.23	0.138	0.361
		2.13	285	1.20	0.162	0.415
KNO ₃ (ii) (2nd heat cycle)	0.595	1.81	405	1.28	0.175	0.405
		1.83	385	1.27	0.173	0.403
		1.84	365	1.27	0.172	0.401
		1.86	345	1.26	0.170	0.399
		1.87	325	1.25	0.168	0.394
		2.13	305	1.23	0.136	0.355
		2.13	285	1.20	0.164	0.420

Table 3**ASTM E1461 Flash Method Thermal Conductivity Results**

Sample	thickness @ 25°C (mm)	bulk density (g/cm ³)	temperature (°C)	specific heat c _p (J/g-K)	diffusivity α (mm ² /s)	conductivity λ (W/m-K)
LiCl-KCl (i) (1st heat cycle)	0.595	1.65	426	1.23	0.299	0.607
		1.66	406	1.19	0.283	0.559
		1.67	386	1.15	0.272	0.522
		1.68	366	1.12	0.260	0.489
		1.69	346	1.08	0.221	0.403
LiCl-KCl (ii) (2nd heat cycle)	0.595	1.65	426	1.23	0.287	0.582
		1.66	406	1.19	0.283	0.559
		1.67	386	1.15	0.277	0.532
		1.68	366	1.12	0.269	0.506
		1.69	346	1.08	0.233	0.425

Table 4**ASTM E1461 Flash Method Thermal Conductivity Results**

Sample	thickness @ 25°C (mm)	bulk density (g/cm ³)	temperature (°C)	specific heat c _p (J/g-K)	diffusivity α (mm ² /s)	conductivity λ (W/m-K)
MgCl ₂ -KCl-NaCl (i) (1st heat cycle)	0.595	1.79	455	1.16	0.135	0.280
		1.80	435	1.12	0.135	0.272
		1.82	415	1.08	0.135	0.265
		1.83	395	1.04	0.130	0.247
		1.85	375	0.980	0.185	0.335
		2.12	355	0.858	0.289	0.526
		2.12	335	0.842	0.291	0.519
MgCl ₂ -KCl-NaCl (ii) (2nd heat cycle)	0.595	1.79	455	1.16	0.159	0.330
		1.80	435	1.12	0.158	0.319
		1.82	415	1.08	0.158	0.311
		1.83	395	1.04	0.153	0.291
		1.85	375	0.980	0.204	0.370
		2.12	355	0.858	0.294	0.535
		2.12	335	0.842	0.294	0.525

Table 5

ASTM E1461 Flash Method Thermal Conductivity Results

Sample	thickness @ 25°C (mm)	bulk density (g/cm ³)	temperature (°C)	specific heat c _p (J/g-K)	diffusivity α (mm ² /s)	conductivity λ (W/m-K)
NaCl-KCl-LiCl (i) (1st heat cycle)	0.595	1.31	423	2.95	0.080	0.309
		1.32	403	2.84	0.081	0.304
		1.34	383	2.80	0.083	0.311
		1.36	363	2.69	0.084	0.307
		1.38	343	2.61	0.090	0.324
		1.91	323	2.19	0.152	0.636
NaCl-KCl-LiCl (ii) (2nd heat cycle)	0.595	1.91	303	2.15	0.158	0.649
		1.31	423	2.95	0.082	0.317
		1.32	403	2.84	0.083	0.311
		1.34	383	2.80	0.085	0.319
		1.36	363	2.69	0.086	0.315
		1.38	343	2.61	0.091	0.328
		1.91	323	2.19	0.154	0.644
		1.91	303	2.15	0.161	0.661

Table 6

ASTM E1461 Flash Method Thermal Conductivity Results

Sample	thickness @ 25°C (mm)	bulk density (g/cm ³)	temperature (°C)	specific heat c _p (J/g-K)	diffusivity α (mm ² /s)	conductivity λ (W/m-K)
Na ₂ CO ₃ -K ₂ CO ₃ -Li ₂ CO ₃ -NaNO ₃ (i) (1st heat cycle)	0.595	2.04	453	1.09	0.203	0.451
		2.06	433	1.08	0.201	0.447
		2.07	413	1.07	0.199	0.441
		2.08	393	1.06	0.198	0.437
		2.09	373	1.05	0.205	0.450
		2.35	353	0.96	0.225	0.508
		2.35	333	0.94	0.240	0.530
Na ₂ CO ₃ -K ₂ CO ₃ -Li ₂ CO ₃ -NaNO ₃ (ii) (2nd heat cycle)	0.595	2.04	453	1.09	0.202	0.449
		2.06	433	1.08	0.201	0.447
		2.07	413	1.07	0.200	0.443
		2.08	393	1.06	0.198	0.437
		2.09	373	1.05	0.202	0.443
		2.35	353	0.96	0.223	0.503
		2.35	333	0.94	0.240	0.530

Figure 11
Specific Heat Estimation for NaCl-KCl-LiCl

Figure 12
Specific Heat Estimation for Na₂CO₃-K₂CO₃-Li₂CO₃-
NaNO₃

Appendix C – Sigma Aldrich Report (Incomplete Draft version)

The attached excel file contains the plots of the data obtained from our DSC run on all the investigated samples. The temperatures associated with transitions observed in each of the DSC measurement cycle (heating and cooling) have been also been tabulated in the same file. The latent heat associated with the transitions has also been listed on each graph.

The table below summarizes the description of the samples corresponding to each of the sample ID's. It is to be noted that in case of the samples with multiple components the numbers in front of the each constituent represent its mole percentage in the sample mixture.

ID	Samples
NS01-21-01	NaNO ₃
NS01-21-02	(80.00)NaOH-(20.00)NaCl
NS01-21-03	(72.34)NaOH-(20.48)NaCl-(7.17)Na ₂ CO ₃
NS01-21-04	KNO ₃
NS01-21-05	(33.00)NaCl-(23.99)KCl-(43.01)LiCl
NS01-21-06	(58.72)LiCl-(41.28)KCl
NS01-21-07	KOH
NS01-21-08	(9.30)K ₂ CO ₃ -(90.70)KOH
NS01-21-09	(50.83)MgCl ₂ -(22.10)KCl-(27.06)NaCl
NS01-21-10	(43.50)Li ₂ CO ₃ -(31.49)Na ₂ CO ₃ -(25.01)K ₂ CO ₃

All the samples were prepared by mixing of the anhydrous/heat treated constituent compounds in a SPEX mill for 30 minutes. For all the samples the following experimental procedure was adopted while collecting the DSC data. The sample was placed in the glove bag, flushed/evacuated 5-times with low

oxygen (<7ppm), N₂. Then the sample was loaded in 2 Mettler-Toledo, gold plated, 40uL, high pressure crucible. The sample was inserted at 20C and then cooled to 0C. The data was collected while ramping up the temperature to 500C at 5C/min. The data was also collected while cooling down to 0C at 5C/min. Then, with the same heating and cooling rates, the data collection was repeated additional 2-times.

The DSC data on the sample NS01-21-01 (NaNO₃; See Fig. 1) indicate that the sample possesses two readily observable transitions at ~270C and ~305C. However, for cycles 2 and 3 the data collected during cooling also show presence of a minor transition at ~220C. Out of the two prominent transitions, the one seen at ~305C shows thermal hysteresis between the data collected during the heating and cooling. This indicates that this transition is of first order character and may be attributed to the solid-liquid phase transition (the melting point of NaNO₃ is ~306C). The latent heat associated with the transition at 305C is estimated to be ~140 J/g.

Fig. 1

During the initial heating of the sample NS01-21-02 [(80.00)NaOH-(20.00)NaCl] (See Fig. 2) three transitions can be noted in the DSC data. The 1st transition peaks at 192C whereas the other two transitions peak at ~209C and 335C. However, during the heating in 2nd and 3rd cycles two prominent transitions peaked at ~204C and 334C can be observed. Thus, the peak seen at 192C in the first heating cycle can be attributed to the reconditioning of the sample during 1st run. A closure inspection of the DSC data near the 2nd and 3rd peaks reveal that each peak contains an additional transition which gets separated (presumably due to the different thermal hysteresis associated with each transformations) resulting in distinct peaks in the data collected during cooling. This results in four distinct peaks in the cooling data collected in 2nd and 3rd cycles. Assuming the neighboring transitions as a single one, the latent heat associated with the transitions at ~209C and 335C is estimated to be ~102 J/g and ~138 J/g, respectively.

Fig. 2

The data on sample NS01-21-03 [(72.34)NaOH-(20.48)NaCl-(7.17)Na₂CO₃] (See Fig. 3) indicates presence of two broad transitions. During the heating cycle the transitions are peaked at ~205C and 316C. The data collected during the heating and cooling cycle show hysteresis. However, the hysteresis associated with the low temperature transition is considerable for this sample. Based on the heating data, the heat associated with the transitions at ~205C and 316C is estimated to be ~73 J/g and ~177 J/g, respectively.

Fig. 3

For the sample NS01-21-04 which is KNO_3 (See Fig. 4), the DSC data collected during 1st cycle appears to be different compared with that collected in 2nd and 3rd cycles. For example the data collected during cooling in cycles 2 and 3 appear to have an additional transition compared to the cooling data from cycle 1. This might be due to reconditioning of the sample during 1st cycle. While the origin of the low temperature peak observed at ~128°C in the data collected during heating is not clear, the peak seen at ~332°C may be attributed to melting of the KNO_3 . The latent heat associated with the solid to liquid transition is ~90 J/g. The appearance of the additional peak in cooling may have origin in the decomposition of the KNO_3 above 400°C during the heating cycle.

[^]exo

NSEL01-21-04, AAPL Ramp, Trial 1

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STAR^e SW 9.01

Fig. 4

The DSC data on the sample NS01-21-05 [(33.00)NaCl-(23.99)KCl-(43.01)LiCl] (See Fig. 5) indicates the presence of only one transition. During the heating the transition peaks at ~360°C whereas during cooling the transition gets broadened and it peaks at ~350°C. The hysteresis in the transition points towards the first order nature of the transition and based on the heating data the latent heat of the transition is estimated to be ~110 J/g.

[^]exo

NSEL01-21-05, AAPL Ramp, Trial 1

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Fig. 5

In case of the NS01-21-06 sample [(58.72)LiCl-(41.28)KCl] (See Fig. 6) two transitions can be seen in both the heating and cooling data. We note that the positions of the peaks associated with the transition vary significantly in data collected during cycle 1 and other cycles. This may be due to reconditioning of the sample during 1st cycle. While the low temperature transition (peaked at ~225C) appears as a kink in the data, associated with the high temperature transition (peaked at ~360C) a distinct peak can be seen. It is to be noted that the width of the high temperature transition reduces significantly leading to a sharp peak in the data collected during cooling. Also, associated with high temperature transition a thermal hysteresis of ~20C is seen between the heating and cooling data. The latent heat associated with the high temperature transition is estimated to be ~195 J/g.

^exo

NSEL01-21-06, AAPL Ramp, Trial 1

05.01.2012 11:48:45

Fig. 6

For the NS01-21-07 sample, which is KOH (See Fig. 7), due to reconditioning of the sample, the DSC data during initial heating show broad transitions which become sharp in the subsequent heating cycle. We note that the data for KOH also show presence of two transitions at $\sim 252^{\circ}C$ and $\sim 407^{\circ}C$ and associated with each transitions there is a thermal hysteresis of $\sim 5^{\circ}C$ between the heating and cooling data. This indicates that both the transitions are of first order nature. The transition seen at $\sim 407^{\circ}C$ is associated with the solid to liquid phase transition of KOH and the latent heat associated with this transition is estimated to be $\sim 110 J/g$.

^exo

NSEL01-21-07, AAPL Ramp, Trial 1

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Fig. 7

The DSC data for the sample NS0-21-08 [(9.30)K₂CO₃-(90.70)KOH] (See Fig. 8) show two transitions peaked at 252°C and 370°C. Associated with both the transitions, the data collected during heating and cooling show a thermal hysteresis. The heat associated with the transitions at 252°C and 370°C is estimated to be ~60 J/g and ~125 J/g, respectively.

Fig. 8

From the DSC data for the sample NS0-21-09 [(50.83)MgCl₂-(22.10)KCl-(27.06)NaCl] (See Fig. 9) it is noted that the data collected during both the heating and cooling protocols show existence of two close phase transitions and, in general, the width of the transition during the heating cycle is more than the one observed during the cooling cycle. Accordingly, the sharpness of the peak associated with the phase transition increases for the data collected during cooling. Furthermore, there is a thermal hysteresis between the data collected during the heating and cooling cycles, which indicates that the phase transition is of first order character. Assuming the two transitions as a single one, the latent heat associated with the transition is estimated to be ~175 J/g.

^exo**NSingh EL)-21, NSEL01-21-01, Trial 1****02.11.2011 06:15:04** **Lab: METTLER****STAR[®] SW 9.01****Fig. 9**

The data for the sample NS01-21-10 [(43.50)Li₂CO₃-(31.49)Na₂CO₃-(25.01)K₂CO₃] (See Fig. 10) one prominent transition which is peaked at ~400C and ~370C during the heating and cooling cycles, respectively. The thermal hysteresis between the heating and cooling data points towards the first order nature of the transition. Based on the cooling data the latent heat associated with the transition is estimated to be ~190 J/g. Apart from a prominent transition, the cooling data also shows existence a broad transition centered about 300C.

^{exo}

NSEL01-21-10, AAPL Ramp, Trial 1

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Lab: METTLER

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Fig. 10

Appendix D – University of Wisconsin Low-Temperature Materials Density Report (Final version)

UW Thermal Hydraulics Laboratory
Internal Report

Date: October 17, 2011

Thermal Hydraulics Laboratory

Precise Measurement of Density of Salt Mixtures

Introduction

Molten salt mixtures containing Nitrates, Hydroxide, Carbonate or Chloride of Sodium (Na), Potassium (K), Lithium (Li) and Magnesium (Mg) can be used as potential heat transfer fluids due to their low melting points. Densities of those molten salt mixtures, depending on the temperature, are useful in the analysis and calculation of such thermal systems. This report describes the experimental results of the densities of molten salt mixtures, listed in Table 1.

Table 1. List of tested salt or salt mixture

Salt or salt mixture, Reagent grade (Mole fraction, %)
NaNO ₃
(80.00)NaOH-(20.00)NaCl
(72.34)NaOH-(20.48)NaCl-(7.17)Na ₂ CO ₃
KNO ₃
(33.00)NaCl-(23.99)KCl-(43.01)LiCl
(58.72)LiCl-(41.28)KCl
KOH
(9.30)K ₂ CO ₃ -(90.70)KOH
(50.83)MgCl ₂ -(22.10)KCl-(27.06)NaCl
(42.89)Li ₂ CO ₃ -(31.31)Na ₂ CO ₃ -(20.34)K ₂ CO ₃ -(5.47)NaNO ₃

Measurement method

The density of molten salts was measured based on the Archimedean principle of buoyancy. The density of a liquid calculated from the buoyancy force acted on a bob immersed in the liquid. The immersed bob is hanged by a wire attached to a high accuracy scale, allowing the determination of buoyancy force by a differential measurement between the immersed mass and resting mass in gas. The density, ρ , of a liquid is calculated according to Equation 1,

$$\rho = \frac{(m_0 - m_i)}{V_0(1 + 3\alpha(T - T_0))} \quad (\text{Eq.1})$$

ρ : Liquid density

T_0 : Ambient temperature

T : Salt temperature at measurement point

m_i : Immersed weight at T

m_0 : Rest weight at T_0

V_0 : Volume of bob at T_0

α : Thermal expansion coefficient of bob

where M_i and M_0 are the masses of the bob immersed in liquid salt and rested in gas at ambient temperature (T_0), respectively, V_0 is the volume of the bob at the ambient temperature, and C is thermal expansion coefficient of the bob material (Nickel). Equation 1 accounts for the correction of V_0 due to expansion of the bob at the temperature of the molten salt, T .

Test apparatus

The apparatus consists of a high accuracy scale, an automatic optical stage controlled by a motor, a testing chamber with a furnace, an alumina crucible as liquid salt container, a nickel bob. Also a vacuum pump, a high pressure Argon gas tank, an automatic pressure controller and a vacuum drying oven are used to assist the experiment. A photograph of the whole apparatus is shown in Figure 1.

An Acculab-Atilon model ATL-224-I scale was used to weigh the bob mass. The measurement range is 0-220 g with 0.1 mg accuracy. This scale has a screw below the transducer which allows weight to be suspended. The scale is sitting in a plane of an optical stage, which can be lifted or lowered down readily through an electrically driven motor. An air flow shield was placed to prevent air convection from interfering scale reading. A vacuum pump and an Argon gas tank are connected to the testing chamber to allow the chamber to be drowned to vacuum condition and back filled with inert gas.

The testing chamber is shown in Figure 2. The chamber can be sealed to allow the vacuum or inert gas condition. There is a glass window on the front side of chamber to allow the observation to the crucible, with the help of a reflect mirror and a light inside. Figure 3 shows the detailed configuration inside the chamber. The molten salt was contained in an alumina crucible with about 150 ml volume capacity. The cylinder shape furnace has a center well about 2.5 inches in diameter and 6 inches in depth, which allow the crucible to sit inside and to be heated by surrounding electrical heaters. The power of heaters is controlled by a SCR connected to the data acquisition computer. Three K type thermocouples are used to record the temperatures of liquid salt, furnace wall and the ambient environment.

Figure 1: Salt Density Test Apparatus.

Figure 2: Testing Chamber with Furnace

Figure 3: Furnace with crucible inside

Figure 4 shows one of the nickel bob. Nickel was chosen as the bob material because its density, 8.908 g/cm^3 at 25°C , is about five times of the expected density of the molten salt mixtures. The coefficient of thermal expansion of nickel is $16.96 \times 10^{-6} \text{ K}^{-1}$ at 327°C . The bob was suspended by stainless steel wire. The correction for the immersed wire was small enough to be negligible. Surface tension forces on the wire connecting the bob is also negligible since the suspending wire is very slim. The calibration of the apparatus and measurement method was confirmed by measuring the density of deionized water and other liquid who has known density. At ambient temperature (20.4°C), a density of 0.997 g/cm^3 was measured compared to the published value of 0.998 g/cm^3 .

Figure 4: Nickel bob and alumina crucible

Figure 5 shows the Yamato vacuum drying oven, Model DP-63. Certain salts are extremely hygroscopic. Those samples must be dried in a vacuum drying oven at high temperature condition with inert gas before testing.

Figure 5: Vacuum drying oven.

Test Procedure

The following general procedures were performed for each experiment:

- Calibrate scale and thermocouples
- Prepare testing sample salt, dry in oven if necessary
- Clean nickel “density bob” and crucible
- Calibrate bob volume with standards
- Fill crucible with desired salt mixture and place into furnace
- Vacuum the testing chamber and back fill with inert gas (N₂)
- Heat salt until melting completely then stabilize temperature
- Record bob weight in inert gas
- Use electrical optical stage to lower bob into salt mixture
- Measure buoyant force on the immersed weight
- Heat liquid salt to next temperature level and record weight
- Repeat for all temperature levels
- Close down facility and examine data.
 - Shut off the program and power supply.
 - Close Argon gas supply
 - Check the oven condition

Test Results (Liquid density)

Table 2 shows the summary of correlation between molten salts density and temperature from the experiment data. The testing results for each salt or salt mixture are presented.

Table 2. Summary of correlation between molten salts density and temperature

No	Salt or salt mixture (mole fraction, %)	Density ρ :[g/cm ³],T:[°C]
1	NaNO ₃	$\rho = 2.140 - 0.7534 \times 10^{-3}T$
2	(80.00)NaOH-(20.00)NaCl	$\rho = 1.977 - 0.5531 \times 10^{-3}T$
3	(72.34)NaOH-(20.48)NaCl-(7.17)Na ₂ CO ₃	$\rho = 2.014 - 0.4948 \times 10^{-3}T$
4	KNO ₃	$\rho = 2.111 - 0.7320 \times 10^{-3}T$
5	(33.00)NaCl-(23.99)KCl-(43.01)LiCl	$\rho = 1.670 - 0.8576 \times 10^{-3}T$
6	(58.72)LiCl-(41.28)KCl	$\rho = 1.861 - 0.4956 \times 10^{-3}T$
7	KOH	$\rho = 1.787 - 0.1707 \times 10^{-3}T$
8	(9.30)K ₂ CO ₃ -(90.70)KOH	$\rho = 1.962 - 0.5201 \times 10^{-3}T$
9	(50.83)MgCl ₂ -(22.10)KCl-(27.06)NaCl	$\rho = 2.110 - 0.7027 \times 10^{-3}T$
10	(42.89)Li ₂ CO ₃ -(31.31)Na ₂ CO ₃ -(20.34)K ₂ CO ₃ -(5.47)NaNO ₃	$\rho = 2.282 - 0.5232 \times 10^{-3}T$

Test Results (Solid density)

Table 3. Summary of solid density

No	Salt or salt mixture (mole fraction, %)	Theoretically* Density ρ :[g/cm ³]	Measured Density ρ :[g/cm ³]
1	NaNO ₃	2.2570	2.2831
2	(80.00)NaOH-(20.00)NaCl	2.1370	2.0050
3	(72.34)NaOH-(20.48)NaCl-(7.17)Na ₂ CO ₃	2.1664	2.0165
4	KNO ₃	2.1090	2.1265
5	(33.00)NaCl-(23.99)KCl-(43.01)LiCl	2.0799	1.9062
6	(58.72)LiCl-(41.28)KCl	2.0333	1.9200
7	KOH	2.0440	2.0760
8	(9.30)K ₂ CO ₃ -(90.70)KOH	2.0669	2.0494
9	(50.83)MgCl ₂ -(22.10)KCl-(27.06)NaCl	2.2036	2.1199
10	(42.89)Li ₂ CO ₃ -(31.31)Na ₂ CO ₃ -(20.34)K ₂ CO ₃ -(5.47)NaNO ₃	2.2895	2.3491

* Theoretically density is calculated based on the mole fraction and reported single salt densities.

**** Comments on Results ****

It was not possible to measure the density to within 10 degree of the melting point for a few of the salt mixtures. This is due to the large oscillations that occur in the achimidian density measurement procedure when solidification begins and the apparent large transition in the melting temperature of the off eutectic salts. As the salts approached the theoretical melting temperature the scale readings oscillated significantly indicating a partial freeze this was also observed visually by the appearance of solidification on the liquid salt surface. In some cases this occurred at temperature 20-30 degree higher than the estimated theoretical melting point. Attempts were made to stir the salt to limit any stratification as the liquid froze but was unsuccessful and confirmed the indication of stratification and freezing differential freezing of the salt mixture. Tests with these salts were repeated multiple times with similar results observed for each test. The estimated uncertainty of the mixture composition is less than 1% molar based on weight measurement uncertainty and vendor specified sample purity. The figure below shows an example of the scale reading (the density fluctuations) that occurs when the salt approached the freezing point.

Figure. Scale reading for KOH density test

Discussion of other sources of error:

1. For some salts, the approximate melting points found in the literature differ from what was provided:

- KOH, Literature^[2] shows 406 °C, vs provided 360 °C

- MgCl₂-KCl-NaCl, Literature^[7] shows 396 °C, vs provided 380 °C

The results from experiments appear to be closer to the literature values than the provided values.

2. Stratification of components could be another reason for the difficulty. As mentioned above the samples were significantly mixed in the liquid state however a few of the mixture with several components seem to separate during the freezing process.

3. *NaCl - KCl - LiCl*, this salt behaves extremely unstable, the test of this salts has been repeated several times and always resulted in unstable reading even when the temperature was significantly higher than the provided melting point (no other literature data was found to confirm the melting point).

Additional observations

The solid density of Salt #6 (LiCl-KCl) has been confirmed to be $1.92 \pm 0.03 \text{ g/cm}^3$, this was also cross-checked by the sample provided by the third party (INL) which has very similar mole fraction composition. The previous low value was believed to be caused by a void that occurred during casting.

NaCl-KCl-LiCl appeared to have the most significant component separation during freezing. When the liquid was stirred at temperature close to 420 C, a sedimentation at the bottom of the crucible was felt also after the test and removal of the solidified salt from the alumina crucible there appeared to be a distinctive layer structure. The next salt that seemed to indicate separation was MgCl₂-KCl-NaCl. Other mixtures, as long as a good mixing was applied before heating, did not show signs of separation upon freezing.

Anecdotal discussion of your observations

a). As mentioned, KOH and NaOH are hygroscopic and need to be kept in a dry container. The NaOH from Sigma is at >98% purity so it did not cause trouble. The KOH, otherwise, is at 90%

(contains H₂O and other impurities), it did turn to paste if stored at 120 C. It was observed that some water-boiling-out like phenomenon from the salt during the heat-up.

b). Most mixtures (excluding the single component salts) need to be heated significantly above the mixture melting temperature in order to form a homogenous liquids mixture. Normally it requires at a minimum temperatures of 30 – 50 C above the estimated melting point to completely melt. The appearance of solidification on the liquid salt surface occurred before expected – generally 20-40 C (and in some cases even 80- 90C in the case - NaCl-KCl-LiCl).

c). Gas coming from the salts seemed to react with the furnace and chamber, especially for NaCl-KCl-LiCl and MgCl₂-KCl-NaCl. The some of the gases caused significant oxidation of the stainless vacuum vessel, which needed to be cleaned after the test.

Images of crucible furnace attacked by salt vapor

d) The alumina crucibles and nickel bob were found to be very resistant to corrosion of the salts. Some mixtures (NaCl-KCl-LiCl and MgCl₂-KCl-NaCl) were found to significantly attack stainless steel and quartz (SiO₂).

We haven't run calculations of the phase diagrams of the specified salts however based on reference ^[7] some of the mixtures tested are fairly far of the eutectics compositions.

Locator #	System	Mol%	T©	Reference
1453	NaCl-Na ₂ CO ₃ -NaOH	6-6.6-87.3	291.0	213
1395	NaCl-Na ₂ CO ₃ -NaOH	7.8-6.4-85.8	282.0	213
1611	NaCl-NaOH	6.3	314.0	1199

From: Physical properties data compilations relevant to energy storage: I. Molten Salts Eutectic data

I few tests in the series were repeated multiple times starting from scratch with the pure salt mixtures and good consistency was found between runs. Exhibiting date that was within the standard error reported below.

Error analysis

-Instrument Accuracy:

ATL-224-I scale: Range is 0-220 g with 0.1 mg accuracy

K Thermocouple: -270 to 1372°C, with ± 2 °C (300-500 °C)

-Error in test:

Uncertainty of Bob volume $\pm 0.005 \text{ cm}^3 / 1.725 \text{ cm}^3$

Uncertainty of hanging wire: $\pm 0.001 \text{ g}$

Uncertainty of neglecting of surface tension: $\pm 0.002 \text{ g}$

Uncertainty of salt weighting on mixing $\pm 0.01 \text{ g} / 80\text{g}$

Uncertainty of submerge depth: $\pm 0.001 \text{ g}$

Uncertainty of unstable reading of scale: $\pm 0.002 \text{ g}$ (up to $\pm 0.2 \text{ g}$ close to melt point.)

Uncertainty of solid piece volume: $\pm 0.25 \text{ cm}^3$

Propagation of error for solid density:

$$\rho = W/V$$

given: $W=W \pm \Delta W$, $V=V \pm \Delta V$

$$\Delta \rho = \sqrt{\left(\frac{\Delta W}{V}\right)^2 + \left(\frac{W \Delta V}{V^2}\right)^2}$$

So if $W = 25.0000 \pm 0.0001 \text{ g}$, $V=15.0 \pm 0.25 \text{ cm}^3$

Since $\Delta W \ll \Delta V$,

$$\Delta \rho \sim W \Delta V / V = 1.67\% \rho, \quad \rho = \rho \pm 1.67\% \rho$$

$$\rho = 1.66 \pm 0.028 \text{ g/cm}^3$$

Propagation of error for liquid density:

Rough estimate overall $\Delta W = \Delta W_1 + \Delta W_2 + \Delta W_3 \dots \sim 0.008 \text{ g}$

If $W = 3.0000 \pm 0.008 \text{ g}$, $V=1.725 \pm 0.005 \text{ cm}^3$

$$\Delta \rho = 0.0098 \text{ g/cm}^3$$

$$\rho \sim \rho \pm 0.01 \text{ g/cm}^3$$

Density of molten salt No. 1:

NaNO_3 : Sodium nitrate, mole number: 85, CAS: 7631-99-4, know melting point: 310 °C

Table 1. Density data points of liquid salt mixture		
Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	2.2831
319.50	592.65	1.9042
341.66	614.81	1.8791
360.90	634.05	1.8648
380.33	653.48	1.8521
401.25	674.40	1.8376
420.10	693.25	1.8262

Figure 1. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 2:

[80.00%, mole] NaOH - [20.00%] NaCl

NaOH: Sodium hydroxide, mole number: 40, CAS: 1310-73-2, known melting point: 318 °C

NaCl: Sodium chloride, mole number: 58, CAS: 7647-14-5, known melting point: 801 °C

Table 2. Density data points of liquid salt mixture		
Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	2.0050
330.2	603.35	1.6505
342.9	616.05	1.7861
359.78	632.93	1.7788
381.65	654.8	1.7667
402.06	675.21	1.7544
421.62	694.77	1.7432

Figure 2. Density data of liquid salt mixture at different temperatures*

* The larger error bar in the point closest to the melting point is associated with the statistical uncertainty in the weight measurement.

Density of molten salt No. 3:

[72.34%, mole] NaOH - [20.48%] NaCl – [7.17%] Na₂CO₃

NaOH: Sodium hydroxide, mole number: 40, CAS: 1310-73-2, known melting point: 318 °C

NaCl: Sodium chloride, mole number: 58, CAS: 7647-14-5, known melting point: 801 °C

Na₂CO₃: Sodium carbonate, mole number: 106, CAS: 497-19-8, known melting point: 851 °C

Table 3. Density data points of liquid salt mixture		
Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	2.0165
329.24	602.39	1.7492
342.36	615.51	1.8400
358.92	632.07	1.8400
378.43	651.58	1.8293
400.70	673.85	1.8159
420.36	693.51	1.8036

Figure 3. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 4:

KNO_3 : Potassium nitrate, mole number: 101, CAS: 7757-79-1, known melting point: 334 °C

Table 4. Density data points of liquid salt mixture		
Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	2.1265
341.80	614.95	1.8771
360.92	634.07	1.8438
379.94	653.09	1.8355
399.12	672.27	1.8199
419.50	692.65	1.8031
440.46	713.61	1.7873

Figure 4. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 5:

[33.00%, mole] NaCl - [23.99%] KCl – [43.01%] LiCl

NaCl: Sodium chloride, mole number: 58, CAS: 7647-14-5, known melting point: 801 °C

KCl: Potassium chloride, mole number: 75, CAS: 7447-40-7, known melting point: 770 °C

LiCl: Lithium chloride, mole number: 42, CAS: 7447-41-8, known melting point: 605 °C

Table 5. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	1.9062
411.74	684.89	1.6212
430.63	703.78	1.6148

449.61	722.76	1.6315
472.3	745.45	1.6280
492.48	765.63	1.6340
509.51	782.66	1.6234

Figure 5. Density data of liquid salt mixture at different temperatures*

*It was not possible to measure densities of this salt closer to the melting point with this method.

Density of molten salt No. 6:

[58.72%, mole] LiCl - [41.28%] KCl

LiCl: Lithium chloride, mole number: 42, CAS: 7447-41-8, known melting point: 605 °C

KCl: Potassium chloride, mole number: 75, CAS: 7447-40-7, known melting point: 770 °C

Table 6. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
------------------	-----------------	------------------------------

21.0 (Solid)	294.15	1.9200
364.40	637.55	1.6783
381.27	654.42	1.6743
400.83	673.98	1.6636
420.93	694.08	1.6522
441.47	714.62	1.6426
461.98	735.13	1.6315

Figure 6. Density data of liquid salt mixture at different temperatures

LiCl(58.72%)-KCl(41.28%)

Density of molten salt No. 7:

KOH

KOH: Potassium hydroxide, mole number: 56, CAS: 1310-58-3, known melting point: 406 °C

Table 7. Density data points of liquid salt mixture		
Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	2.076
404.17	677.32	1.6841
420.75	693.90	1.7152
443.20	716.35	1.7115
461.88	735.03	1.7081
479.32	752.47	1.7041
496.03	769.18	1.7030

Figure 7. Density data of liquid salt mixture at different temperatures*

**The provided melting differs from the literature^[2]: 360 °C vs 406 °C it appears that the 406 value seems closer*

Density of molten salt No. 8:

[9.30%, mole] K₂CO₃ – [90.70%] KOH

K₂CO₃: Potassium carbonate, mole number: 138, CAS: 584-08-7, known melting point: 891 °C

KOH: Potassium hydroxide, mole number: 56, CAS: 1310-58-3, known melting point: 406 °C

Table 8. Density data points of liquid salt mixture		
Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	2.0494
375.68	648.83	1.7670
381.23	654.38	1.7636
403.86	677.01	1.7515
421.2	694.35	1.7435
441.53	714.68	1.7327
461.74	734.89	1.7233

Figure 8. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 9:

[50.83 %, mole] MgCl₂ – [90.70 %] KCl – [27.06] NaCl

MgCl₂: Magnesium chloride, mole number: 95, CAS: 7786-30-3, known melting point: 714 °C

KCl: Potassium chloride, mole number: 75, CAS: 7447-40-7, known melting point: 770 °C

NaCl: Sodium chloride, mole number: 58, CAS: 7647-14-5, known melting point: 801 °C

Table 9. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	2.1199
403.39	676.54	1.7941
417.41	690.56	1.7867

430.9	704.05	1.8062
441.53	714.68	1.8018
461.27	734.42	1.7871
478.38	751.53	1.7735

Figure 9. Density data of liquid salt mixture at different temperatures*

*The provided melting point is different from the literature^[7]: 380 °C vs 396 °C

Density of molten salt No. 10:

[42.89%, mole]Li₂CO₃ - [31.31%] Na₂CO₃ - [20.34%] K₂CO₃ - [5.47%] NaNO₃

Li₂CO₃: Lithium carbonate, mole number: 74, CAS: 554-13-2, known melting point: 723 °C

Na₂CO₃: Sodium carbonate, mole number: 106, CAS: 497-19-8, known melting point: 851 °C

K₂CO₃: Potassium carbonate, mole number: 138, CAS: 584-08-7, known melting point: 891 °C

NaNO₃: Sodium nitrate, mole number: 85, CAS: 7631-99-4, known melting point: 308 °C

Table 10. Density data points of liquid salt mixture		
Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	2.3491
434.16	733.45	2.0123
452.75	725.9	2.0457
459.5	747.23	2.0432
483.63	757.07	2.0289
501.17	771.3	2.0219
520.88	793.09	2.0100

Figure 10. Density data of liquid salt mixture at different temperatures
 $\text{Li}_2\text{CO}_3(42.89\%)$ – $\text{Na}_2\text{CO}_3(31.31\%)$ – $\text{K}_2\text{CO}_3(20.34\%)$ – $\text{NaNO}_3(5.47\%)$

Reference

- [1] Assessment of candidate molten salt coolants for the NGNP/NHI Heat-Transfer Loop, Williams D. F ORNL/TM-2006/69, 2006
- [2] CRC Handbook of Chemistry and Physics (86th ed.). Lide, D. R., ed (2005). Boca Raton (FL): CRC Press. p. 4-80. ISBN 0-8493-0486-5.
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- [4] Electrical conductance and density of molten salt Systems : KCl-LiCl, KCl-NaCl and KCl-KI E. R. Van Artsdalen and I. S. Yaffe, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1954
- [5] Measurement of the thermal-expansion coefficient of nickel from 300 to 1000 K and determination of the power-law constants near the curie temperatures, T. G. Kollic, *Physical Review B*, Vol 16, No 11, 1977
- [6] Molten Salts: Volume 3 Nitrates, Nitrites, and mixtures, Electrical conductance, density viscosity, and surface tension data. G. J. Janz et al., *Journal of physical and chemical reference data*, Vol 1, No. 3, 1972
- [7] Physical properties data compilations relevant to energy storage. I. Molten salts: Eutectic data, George J. Janz et al., NSRDS-NBS-61-1.,1978
- [8] Precise measurement of density and surface tension at temperature up to 1000C in one apparatus, George J. Janz and Max R. Lorenz, *The Review of Scientific Instruments*, 1960.

APPENDIX

Data comparison with literature and reproducibility:

Density of molten salt No. 1:

[Ref]

Molten Salts: Volume 3 Nitrates, Nitrites, and mixtures, Electrical conductance, density viscosity, and surface tension data. G. J. Janz et al., *Journal of physical and chemical reference data*, Vol 1, No. 3, 1972

Density of molten salt No. 2:

NaOH-NaCl

* *Red* and *Blue* are from two tests at UWM

Density of molten salt No. 3:

NaOH-NaCl-Na₂CO₃

* *Red and Blue* are from two tests at UWM

Density of molten salt No. 4:

KNO_3 : Potassium nitrate, mole number: 101, CAS: 7757-79-1, known melting point: 334 °C

[Ref]

Precise measurement of density and surface tension at temperature up to 1000°C in one apparatus, George J. Janz and Max R. Lorenz, *The Review of Scientific Instruments*, 1960.

Density of molten salt No. 6:
[58.72%, mole] LiCl - [41.28%] KCl

[Ref 1]

Electrical conductance and density of molten salt systems : KCl-LiCl, KCl-NaCl and KCl-KI
 E. R. Van Artsdalen and I. S. Yaffe, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1954

*with a mole fraction of [58.80%] LiCl, [41.20%] KCl

[Ref 2]

$$\rho_{[\text{g/cm}^3]} = 1.8772 - 0.87 \times 10^{-3} T_{[^\circ\text{C}]}$$

Williams D. F., "Assessment of candidate molten salt coolants for the NGNP/NHI Heat-Transfer Loop" ORNL/TM-2006/69, 2006

*with a mole fraction of [59.5%] LiCl, [40.5%] KCl

Density of molten salt No. 7:

KOH

* *Red* and *Blue* are from two tests at UWM

Density of molten salt No. 9:

MgCl₂-KCl-NaCl

* *Red* and *Blue* are from two tests at UWM

UW Thermal Hydraulics Laboratory

Internal Report

Date: July 6, 2012

Appendix E – University of Wisconsin High-Temperature Materials Density Report (Final version)

THE UNIVERSITY
of
WISCONSIN
MADISON

Thermal Hydraulics Laboratory

**Measurement of Density of
Liquid Salt and Metal Mixtures (2012)**

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Introduction

Molten salt mixtures containing nitrates, hydroxides, carbonates, fluorides or chlorides of sodium (Na), potassium (K), lithium (Li) and magnesium (Mg), or metal alloys such as aluminum (Al), magnesium (Mg), zinc (Zn), copper (Cu) and silicon (Si) can be used as potential heat transfer and thermal storage medium. The densities of these molten salt mixtures, which depend on the temperature, are necessary for the analysis of such thermal systems. This report describes the experimental results of the densities of molten salt and metal mixtures, listed in Table 1 obtained with the Archimedean methodology.

Table 1. List of tested mixtures

No.	Mixtures (Mole fraction %, unless specified)
1	KCl - MgCl ₂ (69.8 – 30.2)
2	CaCl ₂ – KCl - MgCl ₂ – NaCl (41.6 - 2.2 - 8.8 - 47.4)
3	CaCl ₂ – KCl – NaCl (50 - 7.25 - 42.75)
4	KCl - CaCl ₂ - MgCl ₂ (31 – 22.5 – 46.5)
5	CaCl ₂ - CaF ₂ – NaF (50 – 1.5 – 48.5)
6	CaCl ₂ – NaCl (52.1 - 47.9)
7	KF - KCl - K ₂ CO ₃ (33 – 44.7 – 22.3)
8	KF – KBr (40 – 60)
9	NaCl - MgCl ₂ (56.9 – 43.1)
10	Li ₂ CO ₃ - Na ₂ CO ₃ - K ₂ CO ₃ (41.3 – 32.6 – 26.1)
11	Al - Mg – Zn (56.8 - 37.4 – 2.4) (by mass)
12	Al – Mg (62.9 - 37.1) (by mass)
13	Al - Si – Cu (68.5 – 5 – 26.5) (by mass)
14	Al- Si (87.8 – 12.2) (by mass)
15	“Zamak” – Zn-Al-Mg (~96.0 ~ 4.0 ~ 0.05) (by mass)
16	Candle Wax

Measurement method

The density of molten salts/metals were measured based on the Archimedean principle of buoyancy. The density of a liquid calculated from the buoyancy force acting on a bob immersed in the liquid. The immersed bob is hung by a wire attached to a high accuracy scale, allowing the determination of buoyancy force by a differential measurement between the immersed mass and resting mass in gas. The density, ρ , of a liquid is calculated according to Equation 1:

$$\rho = \frac{(m_0 - m_i)}{V_0(1 + 3\alpha(T - T_0))} \quad (\text{Eq.1})$$

ρ : Liquid density

T_0 : Ambient temperature

T : Salt temperature at measurement point

m_i : Immersed weight at T

m_0 : Rest weight at T_0

V_0 : Volume of bob at T_0

α : Thermal expansion coefficient of bob

where M_i and M_0 are the masses of the bob immersed in liquid salt and rested in gas at ambient temperature (T_0), respectively. V_0 is the volume of the bob at the ambient temperature, and α is thermal expansion coefficient of the bob material (nickel, or others). Equation 1 accounts for the correction of V_0 due to expansion of the bob at the temperature of the molten salt, T .

Test apparatus

The apparatus consists of a high accuracy scale, an automatic optical stage controlled by a motor, a testing chamber with a furnace, and alumina/nickel crucible as liquid salt container, a nickel, stainless steel, alumina or titanium bob. Also a vacuum pump, a high pressure argon gas tank, an automatic pressure controller and a vacuum drying oven are used to assist the experiment. A photograph of the whole apparatus is shown in Fig. 6.

An Acculab-Atilon model ATL-224-I scale was used to weigh the bob mass. The measurement range is 0-220 g with 0.0001 g accuracy. This scale has a screw below the transducer which allows weight to be suspended. The scale is sitting in a plane of an optical stage, which can be lifted or lowered down readily through an electrically driven motor. An air flow shield was placed to prevent air convection from interfering with the scale reading. A vacuum pump and an argon gas tank are connected to the testing chamber to allow the chamber to be brought to vacuum condition and back filled with inert gas.

The testing chamber is shown in Fig. 7. The chamber can be sealed to allow the vacuum or inert gas condition. There is a glass window on the front side of chamber to allow the observation of the crucible, with the help of a reflective mirror and a light. Fig. 8 shows the detailed configuration inside the chamber. The molten salt was contained in an alumina or nickel crucible with about 150 cm³ volume capacity. Fig. 9 shows nickel and alumina crucibles. The cylinder shape furnace has a center well of approximately 2.5 inches in diameter and 6 inches in depth, which allow the crucible to sit inside and to be heated by surrounding electrical heaters. The power of heaters is controlled by a SCR connected to the data acquisition computer. Three K type thermocouples are used to record the temperatures of liquid, furnace wall and the ambient environment.

Fig. 6. Salt density test apparatus.

Fig. 7. Testing chamber with furnace

Fig. 8. Furnace with crucible inside

Fig. 9. Nickel and alumina crucibles

Several types of bobs were used in the density measurement test: nickel, macor ceramic, stainless steel and pure alumina. Fig. 10 shows the nickel and macor ceramic bobs. Nickel was chosen as the primary bob material because its density, 8.908 g/cm^3 at 25°C , is about five times of the expected density of most molten salt mixtures. The thermal expansion coefficient of nickel is $16.69 \times 10^{-6} \text{ K}^{-1}$ at 500°C . The ceramic, alumina or steel bob is used on some mixtures which are corrosive to the nickel (metal alloys). The coefficient of thermal expansion of ceramic (macor) is $9.3 \times 10^{-6} \text{ K}^{-1}$ at 300°C . The coefficient of thermal expansion of stainless steel is $19.5 \times 10^{-6} \text{ K}^{-1}$ around 500°C . The bob was suspended by a thin stainless steel wire. The correction for the immersed wire was small enough to be negligible. Surface tension forces on the wire connecting the bob is also negligible since the suspending wire diameter is very small. The calibration of the apparatus and measurement method was confirmed by measuring the density of deionized water, ethanol and carbon tetrachloride.

Fig. 10. Nickel and ceramic bobs

Fig. 11 shows the Yamato vacuum drying oven, Model DP-63. Certain salts are extremely hygroscopic. Those samples must be dried in a vacuum drying oven at high temperature condition with inert gas before testing.

Fig. 11. Vacuum drying oven.

Test procedure

The following general procedures were performed for each experiment:

- Calibrate scale and thermocouples
- Prepare testing sample salt, dry in oven if necessary
- Clean density bob and crucible

For nickel crucible, wash with acid (oakite/nitric), clean in ethanol, ultrasonically clean in distilled water, dry thoroughly

- Calibrate bob volume with standards (water, ethanol, carbon tetrachloride)
- Fill crucible with desired salt mixture and place into furnace
- Vacuum the testing chamber (~27 mmHg) and back fill with inert gas (argon)
- Heat salt until melting completely then stabilize temperature
- Record bob weight in inert gas
- Use electrical optical stage to lower bob into salt mixture
- Measure buoyant force on the immersed weight
- Heat liquid salt to next temperature level and record weight
- Repeat for all temperature levels
- Cast liquid to a solid piece to measure solid density, store solid salts in sealed jars.
- Close down facility and examine data.
 - Shut off the program and power supply.
 - Close argon gas supply
 - Check the oven condition

Test results

Table 2 shows the summary of correlations between liquid density and temperature from the experiment. The testing results for each mixture are presented in the following section in detail.

Table 2. Summary of correlations of density to temperature

No.	Mixtures (Mole fraction %)	Liquid Density ρ :[g/cm ³], T:[°C]	Solid Density [g/cm ³]
1	KCl - MgCl ₂ (69.8 – 30.2)	$\rho=1.700-1.560\times10^{-4}T$	2.1733
2	CaCl ₂ – KCl - MgCl ₂ – NaCl (41.6 - 2.2 - 8.8 - 47.4)	$\rho=2.079-2.882\times10^{-4}T$	2.2932
3	CaCl ₂ – KCl – NaCl (50 - 7.25 - 42.75)	$\rho=2.202-4.974\times10^{-4}T$	2.1147
4	KCl - CaCl ₂ - MgCl ₂ (31 – 22.5 – 46.5)	$\rho=2.133-6.338\times10^{-4}T$	2.1532
5	CaCl ₂ - CaF ₂ – NaF (50 – 1.5 – 48.5)	NA	NA
6	CaCl ₂ – NaCl (52.1 - 47.9)	$\rho=2.026-3.284\times10^{-4}T$	2.0775
7	KF - KCl - K ₂ CO ₃ (33 – 44.7 – 22.3)	$\rho=2.215-5.983\times10^{-4}T$	2.3605
8	KF – KBr (40 – 60)	$\rho=3.190-17.40\times10^{-4}T$	2.7163
9	NaCl - MgCl ₂ (56.9 – 43.1)	$\rho=2.586-16.58\times10^{-4}T$	2.1069
10	Li ₂ CO ₃ - Na ₂ CO ₃ - K ₂ CO ₃ (41.3 – 32.6 – 26.1)	$\rho=2.230-5.768\times10^{-4}T$	2.2011
11	Al - Mg – Zn (56.8 - 37.4 – 2.4) (by mass)	$\rho=2.332-4.734\times10^{-4}T$	2.2589
12	Al – Mg (62.9 - 37.1) (by mass)	$\rho=2.446-6.844\times10^{-4}T$	2.2285
13	Al - Si – Cu (68.5 – 5 – 26.5) (by mass)	$\rho=3.531-8.305\times10^{-4}T$	3.2517
14	Al- Si (87.8 – 12.2) (by mass)	$\rho=2.671-3.151\times10^{-4}T$	2.6628
15	“Zamak“ – Zn-Al-Mg (~96.0 ~ 4.0 ~ 0.05) (by mass)	$\rho=6.534-9.024\times10^{-4}T$	6.7382
16	Candle Wax	$\rho=0.8131-6.088\times10^{-4}T$	0.8905

General discussion

Measurement close to the expected melting point

For some mixtures, it was difficult to measure the density within 10 degrees of the given melting point as requested. This is due to the large oscillations that occur in the Archimedean density measurement procedure when solidification begins and the apparent large transition in the melting temperature of the off-eutectic salts. Most tests were performed by collecting data points while the liquid temperature was raised step by step. For those mixtures which appeared to need a higher temperature than the expected melting point to melt, the liquid temperature decay process was also monitored to try to get some additional data points at the temperature as low as

possible. As the salts/alloys approached the theoretical melting temperature the scale readings oscillated significantly indicating a partial freeze this was also observed visually by the appearance of solidification on the liquid salt surface. In some cases this occurred at temperature 40-50 degree higher than the estimated theoretical melting point. Attempts were made to stir the salt to limit any stratification as the liquid froze but was unsuccessful and confirmed the indication of stratification and freezing differential freezing of the salt mixture. Tests with these salts were repeated multiple times with similar results observed. The estimated uncertainty of the mixture composition is less than 1% molar based on weight measurement uncertainty and vendor specified sample purity. Fig. 12 shows an example of the scale reading (the density fluctuations) that occurs when the salt approached the freezing point.

Fig. 12. Scale reading for a density test

Data points

For some mixtures, we did not get six data points in a 0 to 125 °C range above the melting point as requested. One reason is that some mixtures need higher temperature than the given melting point to melt down so the whole temperature range was elevated. Sometimes the thin stainless steel hanging wire which was used to hang the bob was corroded at high temperature so the test was terminated unexpectedly. In some cases the salt mixture did not melt well and it was

necessary to repeat the tests with significant pulverizing. Some mixtures, especially the alloys, only have data points in a shorter range of temperature due to the temperature limitation of test equipment.

Pulverizing effect

Most samples we obtained from Sigma are in fine particles and could readily be mixed. However, two samples, NaCl and CaF₂, which are in relatively large particles, were pulverized with an alumina mortar and pestle before mixing. The pulverizing was confirmed to be helpful on the melting process of salt mixture No.6 and No 9, which did not melt well initially. In the repeat run test with proper pulverizing, the salts melted well and reasonable data was acquired. However, even with pulverizing, the No.5 salt mixture was not melting well at high temperature (up to 650 °C) for three runs so the data for mixture No. 5 was not possible.

Fig. 13. Alumina mortar and pestle

Corrosion

Some salt mixtures, especially those containing fluoride (NaF, KF, or CaF₂), are corrosive to the alumina so nickel crucibles were used. A few of these salts are also corrosive to the nickel at elevated temperatures. It has been reported by researchers, that the fluoride molten salts was corrosive to nickel ^[10]. No.5, No.7 and No. 8 showed some corrosion to nickel crucible. “The

impurities in salt such as oxides, sulfur, and metal could result in the deposition of solid particles. Sulfur is corrosive attack on nickel-base alloys at operational temperature.” The liquid metals are also corrosive to some candidate materials which were used to make the bob or crucible. *“Nickel has been characterized as active with both liquid and solid aluminum”* ^[14]. Also, stainless steel is reported to be subjected to corrosion in the liquid metal alloys. This corrosion, even though fairly slow, may result in higher uncertainties to the measurements.

Liquid metal attached to the bob

During the test, the bob was immersed into the liquid metal, when the bob was lifted out of the liquid metal, some liquid metal attached to the surface of bob. There is no easy way to clean it out completely, so multiple bobs were made to finish the tests. Ceramic or alumina bobs were used for some liquid metal, but due to the low density of ceramic, it is not applicable for some of the mixtures. Fig. 14 shows the bob that was highly wetted by the liquid metal.

Fig. 14. Liquid metal attached to the bob after test

Surface tension of liquid metal

The liquid metal, compared to the molten salt, generally has a larger surface tension. Sometimes the surface tension can hold the bob (even those with a higher density) on the liquid surface to prevent it from submerging. Occasionally a little gravitational “drop in” method was utilized to allow the bob to sink into the liquid metal, e.g., the bob was manually lifted by a short elevation

and then was released to let the bob fall into the liquid with a little acceleration. Generally, the uncertainty of the density measurement of liquid metal is expected to be larger than the molten salt due to the higher surface tension and viscosity that influenced the measurements. It was found to not be possible for the Archimedean method to obtain meaningful density measurements at temperatures within 30-60 °C of the melting point for the alloys.

Preliminary data verification.

Due to the lack of literature reference, the direct comparison of the current measurements with literature data was not possible. A theoretical density of the metal mixture was calculated based on a standard mixing rule and density of each single metal composition. This gives a check on the accuracy of the experiment data.

Table 3. Data verification with theoretical value of metal

No.	Mixtures	Liquid Density [g/cm ³]			Solid Density [g/cm ³]		
		Theoretical	Experiment	Error	Theoretical	Experiment	Error
11	Al - Mg – Zn	2.0170	2.0772	2.98%	2.2522	2.2589	0.30%
12	Al – Mg	2.0038	2.0583	2.72%	2.2400	2.2285	-0.51%
13	Al - Si – Cu	2.9333	3.0170	2.85%	3.2807	3.2517	-0.88%
14	Al- Si	2.3972	2.4762	3.30%	2.6485	2.6628	0.54%
15	“Zamak” Zn-Al-Mg	6.1276	6.0802	-0.77%	6.6898	6.7382	0.72%
16	Candle Wax				0.9	0.8905	

*Theoretical density is calculated with standard density model of based on the composition and mass fractions, it may not represent the mixture density exactly, but can be a basic reference.

$$\rho_m = \frac{\rho_1 V_1 + \rho_2 V_2 + \rho_3 V_3}{V_1 + V_2 + V_3} = \frac{m_1 + m_2 + m_3}{V_1 + V_2 + V_3} \quad (\text{Eq.2})$$

Error analysis

ATL-224-I scale: Range is 0-220 g with 0.1 mg accuracy

K Thermocouple: -270 to 1372°C , with $\pm 2^{\circ}\text{C}$ (300 - 500°C)

Uncertainty of bob volume $\pm 0.005\text{ cm}^3/1.725\text{ cm}^3$

Uncertainty of hanging wire: $\pm 0.001\text{ g}$

Uncertainty of neglecting of surface tension: $\pm 0.002\text{ g}$

Uncertainty of salt weighting on mixing $\pm 0.01\text{ g}/80\text{ g}$

Uncertainty of submerge depth: $\pm 0.001\text{ g}$

Uncertainty of unstable reading of scale: $\pm 0.002\text{ g}$ (up to $\pm 0.2\text{ g}$ close to melt point.)

Uncertainty of solid piece volume: $\pm 0.25\text{ cm}^3$

Propagation of error for solid density:

$$\rho = W/V$$

given: $W=W\pm\Delta W$, $V=V\pm\Delta V$

$$\Delta\rho = \sqrt{\left(\frac{\Delta W}{V}\right)^2 + \left(\frac{W\Delta V}{V^2}\right)^2} \quad (\text{Eq.3})$$

So if $W = 25.0000 \pm 0.0001\text{ g}$, $V=15.0 \pm 0.25\text{ cm}^3$

Since $\Delta W \ll \Delta V$,

$$\Delta\rho \sim W\Delta V/V = 1.67\% \rho, \quad \rho = \rho \pm 1.67\% \rho$$
$$\rho = 1.66 \pm 0.028\text{ g/cm}^3$$

Propagation of error for liquid density:

Rough estimate overall $\Delta W = \Delta W_1 + \Delta W_2 + \Delta W_3 \dots \sim 0.008\text{ g}$

If $W = 3.0000 \pm 0.008\text{ g}$, $V=1.725 \pm 0.005\text{ cm}^3$

$$\Delta\rho = 0.0098\text{ g/cm}^3$$
$$\rho \sim \rho \pm 0.01\text{ g/cm}^3^*$$

* In general, the uncertainties of density data for liquid metal would be a little larger due to the greater surface tension and higher viscosity.

Data sheets of each mixture

Density of molten salt No. 1

KCl - MgCl₂ (69.8 - 30.2)

Table 1. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0	294.15	2.1733
440.4	592.65	1.6381
465.7	614.81	1.6243
489.26	634.05	1.6187
515.64	653.48	1.6183
538.65	674.40	1.6168
564.25	693.25	1.6157

Figure 1. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 2

CaCl₂ – KCl - MgCl₂ – NaCl (41.6 - 2.2 - 8.8 - 47.4)

Table 2. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0	294.15	2.2932
531.25	804.4	1.9277
551.5	824.65	1.9231
583.8	856.95	1.9034
606.25	879.4	1.9002
615.4	888.55	1.9062
650	923.15	1.8938

Figure 2. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 3

CaCl₂ – KCl - NaCl (50 - 7.25 - 42.75)

Table 3. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.1147
539.06	812.21	1.9340
564.21	837.36	1.9209
588.35	861.5	1.9082
614.15	887.3	1.8975
640.78	913.93	1.8834
664.1	937.25	1.8710

Figure 3. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 4

KCl - CaCl₂ - MgCl₂ (31 – 22.5 – 46.5)

Table 4. Density data points of liquid salt mixture		
Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.1532
496.2	769.35	1.8327
522.5	795.65	1.7957
547.69	820.84	1.7770
572.55	845.7	1.7597
597.33	870.48	1.7545
621.95	895.1	1.7500

Figure 4. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 5

The data of this mixture was not possible due to significant issues with melting.

Table 5. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21.0 (Solid)	294.15	

Figure 5. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 6

CaCl₂ - NaCl (52.1 - 47.9)

Table 6. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.0775
508.51	781.66	1.8583
525.26	798.41	1.8546
550.3	823.45	1.8458
575.48	848.63	1.8365
600.12	873.27	1.8286
625.61	898.76	1.8210

Figure 6. Density data of liquid salt mixture at different temperatures

Density of molten salt No. 7

KF - KCl - K₂CO₃ (33 – 44.7 – 22.3)

Table 7. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.3605
559	832.15	1.8772
575.48	848.63	1.8753
600.86	874.01	1.8562
625.67	898.82	1.8409
647.4	920.55	1.8255
675.2	948.35	1.8122

Figure 7. Density data of liquid salt mixture at different temperatures*

Density of molten salt No. 8

KF - KBr (40 – 60)

Table 8. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.7163
595.6	868.75	2.1553
600.1	873.25	2.1453
610.52	883.67	2.1277
619.6	892.75	2.1070
634.2	907.35	2.0891

Figure 8. Density data of liquid salt mixture at different temperatures*

*The mixture had serious corrosion issues so limited data points were acquired (as seen in Appendix III). The 595 °C is the lowest possible point meaningful data could be collected.

Density of molten salt No. 9

NaCl - MgCl₂ (56.9 – 43.1)

Table 9. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.1069
487.5	760.65	1.7750
513	786.15	1.7350
537.62	810.77	1.7000
557.26	830.41	1.6650
574.24	847.39	1.6267

Figure 9. Density data of liquid salt mixture at different temperatures*

Density of molten salt No. 10

Li₂CO₃ - Na₂CO₃ - K₂CO₃ (41.3 – 32.6 – 26.1)

Table 10. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.2011
494.03	767.18	2.0074
525.45	798.6	2.0016
550.38	823.53	1.9886

575.42	848.57	1.9715
599.25	872.4	1.9503
624	897.15	1.9373

Figure 10. Density data of liquid salt mixture at different temperatures

Density of molten metal No. 11

Al - Mg - Zn (56.8 - 37.4 - 2.4)

Table 11. Density data points of liquid metal mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.2589
490.97	764.12	2.1521
520.5	793.65	2.0867
538.04	811.19	2.0772
562.05	835.2	2.0643

591.6	864.75	2.0506
616.39	889.54	2.0417

Figure 11. Density data of liquid metal mixture at different temperatures

Density of molten metal No. 12

Al - Mg (62.9 - 37.1)

Table 12. Density data points of liquid metal mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.2285
520.2	793.35	2.1164
543.51	816.46	2.0708
557.5	830.85	2.0673
570.3	843.6	2.0583
583.64	856.26	2.0477
602.7	875.85	2.0316

Figure 12. Density data of liquid metal mixture at different temperatures. **Based on the temperature curves the melt point seems to be consistent with the expected. However the increase in the viscosity and surface tension of the metal cause the Archimedes method for density measurement to become inaccurate even within 70C of the melt point.**

Density of molten metal No. 13

Al - Si - Cu (68.5 – 5 – 26.5)

Table 13. Density data points of liquid metal mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	3.2517
585.35	858.5	3.0514
600.19	873.34	3.0240
613.88	887.03	3.0170
631.56	904.71	3.0110
648.55	921.7	3.0025

Figure 13. Density data of liquid metal mixture at different temperatures

No 13. Al – Si – Cu (68.5 – 5 – 26.5)

Density of molten metal No. 14

Al- Si (87.8 – 12.2)

Table 14. Density data points of liquid metal mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	2.6628
586.38	859.53	2.4878
602.36	875.51	2.4803
615.3	888.45	2.4762
630.11	903.26	2.4723
648.5	921.65	2.4672

Figure 14. Density data of liquid metal mixture at different temperatures*

*The FactSage data shows the expected melting point is around 580 °C, which is consistent with the thermocouple temperature measurements shown in figure 29. The density measurement at this point close to this melting point has large error due to proximity to the melting point as with the other alloy mixtures.

Density of molten metal No. 15

Zn-Al-Mg (~96.0 ~ 4.0 ~ 0.05)

Table 15. Density data points of liquid metal mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	6.7382
432.02	705.17	6.2140
457	730.15	6.1156
486.93	760.08	6.0990
509	782.15	6.0802
525.06	798.21	6.0603
548.85	822	6.0334

Figure 15. Density data of liquid metal mixture at different temperatures

As previously stated while it appears that the metals are melting at the expected temperature, based on thermocouple measurements it was not possible to obtain accurate density measurements within approximately 60°C of the melting point.

Density of No. 16

Candle Wax

Table 16. Density data points of liquid salt mixture

Temperature (°C)	Temperature (K)	Density (g/cm ³)
21	294.15	0.890526
75.6	348.75	0.7659
103.65	376.8	0.7493
133.08	406.23	0.7338
156.28	429.43	0.7198
184.5	457.65	0.7009
205.14	478.29	0.6863

Figure 16. Density data of wax at different temperatures

Appendix. I. Comments on issues associated with density measurements of some mixtures.

No. 1. KCl - MgCl₂ (69.8 – 30.2)

This binary mixture melted as expected. The data points were acquired within 10 degree of expected melting point. There is some reference about (KCl – MgCl₂) with a composition of 67-33 mole %, which is close to the present test sample. The formulation given in the literature for this mixture was found to be:

$$\rho = 2000.7 - 0.45709T \text{ [kg/m}^3\text{]} (1030\text{--}1140 \text{ K}) (\text{Janz})^{[12]}. \text{ (for 67-33 mole\%)}$$

A comparison of this literature data is shown in Fig. 15. The disagreement is caused by different mole fraction and temperature application range.

Fig. 15. Comparison with literature of Salt No.1

No.2. CaCl₂ – KCl - MgCl₂ – NaCl (41.6 - 2.2 - 8.8 - 47.4)

The melting of this mixture occurred at a temperature higher than the expected melting point. We were able to get the first data point around 525 °C.

No.3. CaCl_2 – KCl - NaCl (50 - 7.25 - 42.75)

The melting of this mixture occurred at a temperature higher than the expected melting point. We were able to get the first data point around 535 °C.

No.4. KCl - CaCl_2 - MgCl_2 (31 – 22.5 – 46.5)

This mixture melted as expected and six data points were obtained.

No.5. CaCl_2 - CaF_2 – NaF (50 – 1.5 – 48.5)

We were not able to get reliable density data on this salt because of the high corrosion to the nickel and alumina density bobs and crucibles. The mixture also did not melt well even with proper pulverizing. The mixture did not melt until a temperature of 650 °C and was consistent with multiple attempts, as shown below.

Fig. 16. Salt No.5 at 650 °C (with pulverizing)

No.6. $\text{CaCl}_2 - \text{NaCl}$ (52.1 - 47.9)

This mixture melted as expected after the pre-mixing pulverizing. The figure below shows mixture No.6 at 650 °C without the pre-mixing pulverizing. The salt was did not melt well due to the high melting point of the individual mixture components. Extensive pulverizing and dry mixing was required to achieve homogenous melting near the literature reported melting point.

Fig. 17. Salt No.6 at 650 °C (without pulverizing)

No.7. $\text{KF} - \text{KCl} - \text{K}_2\text{CO}_3$ (33 – 44.7 – 22.3)

The fluoride is reported to be corrosive to the alumina so the nickel crucible was used for No. 7 (also for No.5 and No.8). The first data point was 30 °C higher than the expected melting point.

No. 8. KF – KBr (40 – 60)

Mixture No. 8 was shown to be highly corrosive to the nickel crucible as seen below. The first data point is about 15 °C higher than the expected melting point. Due to the high corrosion effect, only a limited number of data points were acquired within a narrow range of temperature. It is not clear what materials would hold up to this mixture at these temperatures. Neither nickel nor high purity alumina were capable to contain this mixture.

Fig. 18. Nickel crucible before and after test with No. 8

No.9. NaCl - MgCl₂ (56.9 – 43.1)

Similar to mixture No. 6, the pre-mixing pulverizing helped the melting process of this mixture. The first data point is about 40 °C higher than the literature expected melting point. The figure below shows the salt mixture No. 9 at 650 °C without the pre-mixing pulverizing. A homogenous mixture was not obtained.

Fig. 19. Salt No.9 at 650 °C (without pulverizing)

No.10. Li_2CO_3 - Na_2CO_3 - K_2CO_3 (41.3 – 32.6 – 26.1)

The first meaningful data point is much higher (about 100 °C) than the expected melting point. Repeat runs have been done to confirm this and resulted in similar results.

No.11. Al - Mg - Zn (56.8 - 37.4 – 2.4)

Generally all the metal alloys appeared to need a temperature significantly above the literature reported melt temperature to obtain reliable density data with the Archimedes density bob procedure. The first reliable data point was obtained at 90 °C higher than the expected melting point for mixture No.11. These metals are easily oxidized and the environment needed to be

highly inert to prevent oxidation. A test with slight oxygen shows a reaction which produced oxides as shown in the figure below.

Fig. 20. Indication of oxidation of No.11

No.12. Al - Mg (62.9 - 37.1)

The first reliable data point was obtained 40 °C higher than the expected melting point. We performed some tests to study the effects of O₂ and air contamination on this mixture. The mixture was found to be highly reactive and resulted in a highly exothermic reaction within air resulting in burning and significant oxide formation as shown in Fig. 21.

Fig. 21. No.12 with oxidation.

No.13. Al - Si - Cu (68.5 – 5 – 26.5)

The first data point for this mixture was obtained 60 °C higher than the expected melting point.

Fig. 22 shows picture of mixture No.13 before and after test.

Fig. 22. Before and after test of No.13

No.14. Al- Si (87.8 – 12.2)

The first meaningful data point for this mixture was obtained 30 °C higher than the expected melting point. Fig. 23 shows the mixture No.14. In this series of tests the wire holding the density bob was broken (due to corrosion) after 5 data points were obtained in a short range of temperature, no further data was possible.

Fig. 23. No.14 after the test

No.15. Zn-Al-Mg (~96.0 ~ 4.0 ~ 0.05)

This is the “heaviest” mixture of all testing samples. Due to the high concentration of zinc, the expected density of this mixture is about 6.8 g/cm³. Generally the density of measuring bob needs to be significantly larger than the liquid in order to obtain good measurement with the Archimedean method. The density of nickel bob is 8.9 g/cm³, however this alloy is corrosive to the nickel so a stainless steel bob with a density about 7.9 g/cm³ was used for these measurements (this caused higher than anticipated errors). Fig. 24 is a photo of mixture No.15.

Fig. 24. No.15 after the test

No.16. Candle Wax

The wax melted as expected as shown in Fig. 25 and was easy to work with and was easy to obtain accurate density measurements

Fig. 25. No.16 after the test (Wax)

Appendix. II. Literature review of the temperature dependence of liquid metals

From Fig. 26 to Fig. 30, the temperature dependence of liquid metals, such as Al, Cu, Si and Zn are shown according to the literature. These metals have a negative slope of density with respect to temperature.

Fig. 26. Temperature dependence of liquid aluminum ^[1]

Fig. 1.—Density of liquid copper.

Fig. 27. Temperature dependence of liquid copper ^[2]

Fig. 28. Temperature dependence of molten silicon ^[11]

Fig. 29. Temperature dependence of molten silicon ^[11]

Figure 3. The density of pure liquid zinc reported here and compared with literature data.

Fig. 30. Temperature dependence of molten zinc ^[13]

Appendix. III. Issues with the Archimedean methodology of density measurements.

The Archimedean principal is a highly accurate straight forward method to obtain the density of most high temperature fluids (HTFs); however some of the proposed HTF's resulted in significant difficulty due to corrosion, high surface tension effects and non-isothermal melting points. For a few salt and most metals mixtures, it was not possible to obtain reliable density measurements in close proximity to the reported melting point temperature.

Fig. 31 shows the temperature transition of the melting and freezing of salt mixture No. 7 as measured by a calibrated k-type thermocouple submersed in the mixture. As can be seen the actual melting and freezing occurred around 555 °C (about 30 °C high than the anticipated literature value). Also evident is the non-isothermal melt and freeze transition.

Fig. 31. Melting and freezing of No. 7

Fig. 32 shows the temperature transient of melting of salt mixture No. 9. In this figure the melt process is seen to occur at approximately 440 °C, but again there appears that the melt transition in non-isothermal and it was only possible to obtain accurate density measurements above 480 °C. There is no data available for the freezing process.

Fig. 32. Melting of No. 9

Fig. 33 shows the temperature transition of melting and freezing of salt mixture No. 10. In this mixture completely melting was not achieved around until 520 °C and freezing was observed around 495 °C. The reason why this melt temperature was significantly higher than expected is not known, but several attempts resulted in similar results.

Fig. 33. Melting and freezing of No. 10

Fig. 34 shows the temperature transition of melting and freezing of metallic mixture No. 14, as can be seen a clear melt and freeze both occurred around 580 °C (this was consistent with the value suggested by FactSage: 850 K). While the melt temperature is consistent to that expected the surface tension increase at temperatures close to the freezing point resulted in significant difficulty in measuring the density and reliable temperatures were not possible near the melt point.

Fig. 34. Melting and freezing of No. 14

Fig. 35 shows the temperature transition of melting and freezing of metallic mixture No. 15. As can be seen the actual melting and freezing both occurred around 383 °C, which is consistent with the expected temperature. While the melt temperature is consistent to that expected the surface tension increase at temperatures close to the freezing point resulted in significant difficulty in measuring the density and reliable temperatures were not possible near the melt point.

Fig. 35. Melting and freezing of No. 15

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[1-15]

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Appendix F – One-Dimensional, Steady State, Thermal Conductivity Enhancement Experiment (Final version)

Executive Summary

This experiment has been designed to determine the effects that expanded metal TCE will have on the bulk thermal conductivity of a substrate material. The experiment is specifically intended to determine material requirements to achieve a TCE ratio of approximately 4x, which is required to optimize PCM systems currently under investigation. The results of this experiment clearly demonstrate that a thermal conductivity enhancement of 4x is possible while keeping the volume and cost of TCE material to a manageable level. For example, approximately 99% of the storage volume of a LHSS may be composed of the storage material, with only 1% of the volume occupied by TCE. The prediction equation and model developed during this experiment fit the data with minimal error and may be used to predict TCE ratio of a test sample that has factor levels similar to those used in this equation.

To supplement the experimental results, an analytical model and a computer simulation have been created to predict the TCE ratio of the test articles used in the experiment. The analytical model has been established using a thermal resistance network simplification and with the assumption of simple conduction heat transfer. This model fits the experimental data loosely, with the error resulting from both experimental variability and oversimplification of the analytical model. The analytical model serves the purpose of roughly verifying the results of the experiment, and further development may be desired to increase accuracy further.

The computer model has been produced using SolidWorks. Each test article manufactured during the experiment has been modeled with SolidWorks and the simulation has been run to compare the experimental results with ideal results. The comparison has determined that the experimental results appear to closely fit the computer simulation results, with the exception of an offset that is most likely attributable to heat loss. Using this estimated heat loss, a new model has been developed to estimate the TCE ratio of each sample by adjusting the heat input to each test article. This model should be verified based on further heat loss experimentation.

The experimental results observed provide a good baseline for further use of expanded metal TCE, however, further experimentation will likely be required to aid in verification of these results and to determine the scalability of the effects seen in this experiment.

Introduction

Background

A thermal energy storage (TES) system employs a large mass of a solid or liquid material that is heated and cooled to store energy. The storage system is “charged” by adding energy to it such that the material’s temperature rises to a desired setpoint. During “discharge”, heat energy is extracted from the tank without removing any of the material through use of heat exchangers.

The design of a thermal energy storage system must consider many material properties in order to satisfy both the performance and the cost effectiveness of the system. If a storage system is to perform well, it must have the ability to pass heat into and out of a storage medium quickly and easily. A system that has this ability has low thermal resistance. Systems have low thermal resistances because of a path of heat transfer containing high conduction and/or convection properties.

The second desirable property sought in a good thermal storage material is a large capacitance, or the ability of the system to absorb and retain large quantities of heat. For example, water can store a large amount of heat for its mass; however, oils can only store only one fourth as much energy, on average. Solids and gasses have similar properties to oils.

In order to develop systems that have these outlined properties, two different types of thermal storage options are available. One option is to transfer heat into and out of the system without the storage material changing phase. For example, the storage material remains as a solid, liquid, or gas during charge and discharge of the system. This type of system is called a sensible heat storage system because the heat transferred into the system serves only to raise the temperature of the storage material.

Conversely, a different type of heat storage system known as a latent heat storage system (LHSS) may be employed. In this type of system, the storage material changes phase during each charge/discharge cycle. Most materials require a large amount of heat to change phase, this heat is known as the latent heat. This property allows increased quantities of energy to be transferred compared to a similarly-sized sensible storage system.

The storage medium used in a LHSS is known as phase change material (PCM). The PCM is contained in one, or several tanks from which immersed heat exchangers are used to transfer energy to and from storage to the HTF. When the heat stored by these systems is generated by a concentrated solar power (CSP) source, the PCM is usually a salt. As heat is transferred into the storage system, the salt melts, and as heat is drawn out of the LHSS, the salt will freeze. A LHSS takes advantage of the latent heat to reduce the total amount of storage material that is required to store a set amount of heat energy. A PCM material is also able to store, or discharge, a large amount of heat at a constant temperature by utilizing latent heat, because the change of phase of a material occurs at a specific temperature. These advantages make PCM a viable option to store thermal energy in a variety of applications, including a solar trough CSP system.

Benefits of Thermal Conductivity Enhancement

A LHSS utilizes the latent heat of fusion of a material for energy storage. This is an effective method for reducing the volume storage system since the energy required to change the phase of a substance can be orders of magnitudes larger than the same materials' ability to store sensible heat. By taking advantage of the latent heat, an equivalent amount of energy can be stored with significantly less storage material. This subsequently reduces the system costs.

One setback for these systems is the relatively low thermal conductivity of the salts most often used as a storage material. Due to the salts low thermal conductivity, the system has a large thermal resistance for transferring heat. The low thermal conductivity of the salts increases the time required to fully charge (melt) and discharge (freeze) the salt because heat flows much more slowly through the storage material. This undesirable material property requires a large heat exchanger surface area in order to counteract the low thermal conductivity so that energy can be passed into and out of the system quickly. This is a very expensive remedy.

A LHSS using salts as the PCM behaves in an analogous fashion to baking a potato. If a baked potato is cooked in an oven for a few minutes, the outside layer gets very hot but the inside is still cold and uncooked. The potato has absorbed a lot of heat but it can't pass the heat to the center of the spud quickly since it has a high thermal resistance. If a skewer or metal rod is placed through the center of the potato, as shown in Figure 36, heat can be quickly passed into its center where the potato can soak up this heat that is being injected directly into its core. By using this skewer, an enhanced thermal conductivity path has been created directly through the center of the potato.

Figure 36: The improvement in heating with a composite system

Thermal conductivity enhancement (TCE) in a LHSS acts similarly to a potato skewer to increase the overall thermal conductivity of the storage material. By effectively increasing thermal conductivity of the PCM through the use of a TCE material, the cost of the storage system is reduced further with a reduction in the amount of required HX surface area required to quickly and completely charge and discharge the system.

One method of TCE is to use sheets of metal that are spaced evenly throughout the phase-changing salt to increase the overall thermal conductivity of the material. One viable sheet-like TCE material is expanded metal, as shown in Figure 37. Aluminum is a wise choice as the TCE material because it has a relatively high thermal conductivity (~4x carbon steel) and it is relatively corrosion resistant. Expanded metal TCE has been chosen because it is a low-cost and widely-produced material. In addition, expanded metal consists of a uniform web of heat conduction paths, making the TCE ratio predictable and easy to implement into the system. In a PCM storage system, the sheets of expanded metal will be suspended in the salt in between the HX plates. Based on separate analysis, it has been determined that approximately a 4x increase in the thermal conductivity, compared with that of the pure salt, will be required to optimize the PCM storage system currently under investigation for current CSP trough plants that use oil-based HTF in the solar field.

Figure 37: Expanded metal similar to that used in this experiment

Experiment Design

Experiment Description

An experiment has been designed to determine the thermal conductivity of a composite material containing a substrate (base material) with thermal conductivity enhancement material embedded within. This test simply measures temperatures within the test specimen and electrical power through a resistance heater to ensure 1-dimensional, steady state heat transfer through the composite material has been reached.

Plain paraffin wax is used as the base material and aluminum, expanded metal is embedded into the wax to increase the thermal conductivity of the composite specimen. A wax test article with embedded TCE is shown in **Figure 38**.

Figure 38: A test article with several sheets of expanded metal (left) and a test article that has been sawed and has ice bath fixed on top (right)

Wax has been selected because of it has a similar thermal conductivity to some of the salts used in a LHSS and due to safety issues associated with handling molten salts near 300°C. The fabrication of each composite test specimens is similar to that of pouring a molded candle. However, the test article must be poured and cooled in multiple stages so that voids do not occur as the wax cools and shrinks. Depending on the particular test configuration, expanded metal is cut into sheets that are placed vertically into the mold prior to pouring the melted wax. The sheets are spaced evenly and are sized to intersect the outside edge of the wax test article at the location they are placed. The expanded metal is oriented so that the long axis of the diamond pattern is vertical. While the thermal conductivity properties of the wax are slightly different than the actual salt PCMs, a baseline measurement of the plain substrate material is used to determine the factor increase in performance of the composite specimen.

The wax test article sits directly on an aluminum puck with a flat adhesive heater placed on the bottom (See Figure 38). An aluminum cylinder is fixed on top of the wax test article to contain the ice bath that is placed in direct contact with the top surface of the wax specimen. The ice bath is agitated with a bubbler to aid in mixing. The test article is insulated and thermocouple probes are inserted, as shown in Figure 40. An electrical, resistance heater is adhered to the bottom surface of the puck and is used as the heat source. The ice bath contained in the aluminum cylinder acts as a constant heat sink at a temperature of 0°C. During the experiment, the heater is kept at a temperature not to exceed 40°C, which is near the melting temperature of the wax. The temperature difference between the source and sink creates a heat flux through the test article. After the system has reached steady state, as determined by the temperature readings of the probes, the assumption is made that all of the heat delivered to the heater is transferred through the test specimen to the ice bath.

Insulation is added around the test article in help direct the heat flow to one dimension; axially through the test specimen. At steady state, the thermal conductivity is determined for the test article using the Fourier's heat conduction equation shown in Figure 39. In this

equation, the q is the heat transfer, in W, L is the length of the heat transfer path, in m, A is the area of the heat transfer path, in m^2 , and ΔT is the temperature difference between the heat source and heat sink, in K. The temperature difference is calculated with the aid of thermocouple probes, which have been inserted into the center of the wax specimen through drilled holes, which are spaced at uniform intervals. The thermal conductivity is calculated using values that are based on two thermocouple probes that are inserted into the wax specimen. By using data from points in the wax specimen, effects at the interface between the wax and the heater puck and the ice bath do not affect the calculated thermal conductivity.

$$k = \frac{q \times L}{A \times \Delta T}$$

Figure 39: The equation used to calculate the thermal conductivity of the composite test article

A detailed experimental procedure may be found in **Appendix F-1 – Experimental Procedure**.

Figure 40: A test article with insulation fixed in place and an ice bath in the top cylinder

It should be noted that several subtle advantages exist because of this experimental design. The use of an axis-symmetric cylindrical shape of the setup eliminates any irregular heat transfer effects that may occur through sharp edges. This also promotes even heat flux through the test article, as well as even heat losses through the side walls of the specimen. The wax test specimen has been removed from the thin, cylindrical aluminum mold in which the test specimen was poured. This would have been a large experimental error as heat could have flowed through this parallel and highly conductive path. The experiment does not require the heating of any material above 40°C , which minimizes the thermal losses from the experiment to the ambient air at approximately 25°C . For each run of the experiment, each test article is observed with the same temperature difference across it to help ensure that thermal losses are relatively equal between the different experiments. In addition, the use of an aluminum puck at the bottom of the test article aids in even heat distribution to the surface of the wax. These experimental advantages serve to increase the overall accuracy and precision of the results.

Experiment Configurations

The expanded metal used in this experiment has acquired from the Alabama Metal Industries Corporation (AMICO). Based on their non-flattened, expanded metal product line, a range of different geometries from the least-dense to the most-dense sheets available are listed in Table 1.

Table 1: The expanded metals used in this experiment

Description	Weight (lbs/C.S.F.)	Size of Openings (in)		Center to Center of Bond (in)		Size of Strand (in)		Percent Open Area	No. of Diamonds per ft ²	Overall thickness (in)
3/4 .125 R AL	65	0.688	1.688	0.923	2	0.17	0.125	66	13	0.305
1 1/2 .125 R AL	43	1.188	2.5	1.333	3	0.163	0.125	78	9	0.3
3/4 .081H R AL	41	0.75	1.688	0.923	2	0.165	0.081	69	13	0.3
1 1/2 .081 R AL	22	1.188	2.5	1.333	3	0.128	0.081	87	9	0.24
1 1/2 .051 R AL	13	1.225	2.4	1.33	3	0.11	0.051	88	9	0.2
3/4 .188 R AL	113	0.59	1.35	0.923	2	0.2	0.188	60	13	0.4

The test matrix of 17 unique configurations from the 6 different materials listed in Table 1 was largely determined based on the software application Design Expert v3.01, produced by Stat-Ease Inc. This program determines optimized combinations of variables that are evenly spaced in the possible design area. This eliminates the need to test every possible combination of variables. The program is also able to fit an empirical model to the experimental data and output a prediction equation for each response variable.

In this experiment, the response variable (or dependent variable) has been identified as the thermal conductivity enhancement. This is the thermal conductivity of the enhanced test article (using a configurations of the expanded metal as the TCE) divided by the thermal conductivity of the plain wax, according to the equation shown in Figure 41. This response variable has been determined to be fully dependent on three independent variables: the expanded metal strand's cross-sectional area (as specified by the manufacturer), the percent open space (as viewed normal to the primary plane of the expanded metal sheet as specified by the manufacturer), and the center-to-center spacing of multiple sheets of expanded metal used in the test specimen. Based on the output of Design Expert, given the ranges of input variables, the experiment has been designed with 20 runs to be carried out with the combination of variables as shown in Table 2. The runs are divided into 17 unique test article configurations. 20 total runs have been performed, with the last four runs consisting of repeats of the same test article configuration.

Table 2: The variable configurations for this experiment

Run	Strand Area (in ²)	Percent Open Space (dec. %)	Spacing (in)
1	0.0104	.87	1
2	0.0134	.69	1.3333
3	0.0056	.88	1
4	0.0204	.78	2
5	0.0213	.66	0.8
6	0.0104	.87	1.3333
7	0.0376	.60	2
8	0.0213	.66	2
9	0.0134	.69	0.8
10	0.0134	.69	2
11	0.0056	.88	1.3333
12	0.0204	.78	0.6667
13	0.0213	.66	1.3333
14	0.0056	.88	0.5714
15	0.0104	.87	0.8
16	0.0376	.60	1
17	0.0204	.78	1
18	0.0204	.78	1
19	0.0204	.78	1
20	0.0204	.78	1

Results

Experimental Results

During the course of this experiment, 20 tests have been carried out. 17 of the test configurations are unique. In addition, the 17th-20th case of the experiment are redundant test specimens for use by Design Expert to determine the number of degrees of freedom needed for an adequate statistical test of the model. The redundant tests are also useful when estimating the experimental error.

The bulk thermal conductivity of each test article was calculated after reaching steady state during the test. Based on numerous tests that quantified the thermal conductivity of pure wax (i.e., without any TCE added) to be 0.56 W/m*K, the TCE is a ratio of the tested thermal conductivity of the enhanced specimen to that of the plain wax. This relationship is shown in Figure 41.

$$TCE = \frac{k_{test\ article}}{k_{plain\ wax}}$$

Figure 41: The relationship used to calculate TCE

As previously stated, the TCE ratio of each test article has been determined to be fully dependent on three independent variables. See Table 3 for a summary of the experimental configurations and results.

Table 3: Summary of experimental configurations and results

Run	Strand Area (in ²)	Percent Open Space (dec. %)	Spacing (in)	Therm. Cond (W/m*K)	TCE
1	0.0104	.87	1	2.607	4.656
2	0.0134	.69	1.3333	3.249	5.802
3	0.0056	.88	1	2.233	3.987
4	0.0204	.78	2	2.252	4.021
5	0.0213	.66	0.8	8.191	14.626
6	0.0104	.87	1.3333	2.293	4.095
7	0.0376	.60	2	3.934	7.025
8	0.0213	.66	2	2.898	5.175
9	0.0134	.69	0.8	4.832	8.628
10	0.0134	.69	2	2.110	3.769
11	0.0056	.88	1.3333	1.459	2.606
12	0.0204	.78	0.6667	6.160	11.000
13	0.0213	.66	1.3333	4.348	7.763
14	0.0056	.88	0.5714	2.975	5.312
15	0.0104	.87	0.8	2.825	5.044
16	0.0376	.60	1	8.149	14.551
17	0.0204	.78	1	3.776	6.743
18	0.0204	.78	1	3.988	7.121
19	0.0204	.78	1	3.826	6.833
20	0.0204	.78	1	3.994	7.132

To perform a statistical analysis on the data, Design Expert software has been used. This software is able to determine a regression and aid in statistically analyzing the goodness-of-fit to the experimental data. A second-order prediction equation has been found to give the best fit. This model is associated with an R² value of .9709, indicating a very good overall fit to the experimental data. After the model has been fit to the data, a statistical analysis is performed to ensure that the model is accurate. Many of the analyses performed by design expert are based on the t-distribution, which is similar to a normal distribution, but with more accuracy for small sample sizes. Each data point may be analyzed independently. A residual between each experimental value and the corresponding regression-predicted value is calculated. In addition, the residual is often normalized based on the associated t-distribution calculated for the data. This value is known as a studentized residual, or "student" residual, and is helpful when comparing the relative fit, as compared to the model regression, of each data point.

Two plots are especially useful in determining model appropriateness. One plot is the normal probability plot of the residuals, which will indicate any patterns in the error term which may be corrected by a data transformation. If the plot shows a linear regression, then the error term shows normality, and the model is likely appropriate. This plot is shown in Figure 42. Another useful graphic is the plot of the residuals versus the experimentally-determined TCE ratio. This plot must indicate no particular pattern, as a clear pattern is an indication that the model does not show a good fit across the entire response range. This plot is shown in Figure 43. Both plots indicate that the quadratic model is appropriate for this data.

Figure 42: A plot showing the normality of the error term. This plot should have a linear regression.

Figure 43: A plot showing the trend of the model residuals versus the experimental TCE ratio

The individual data points may be analyzed to determine outliers based on the output shown in **Table 4**. For this model, a t-value describing the residual of each data point of above 3.5-4.0 should be considered an outlier. None of the data points in this experiment are determined to be outliers based on this criterion.

Table 4: Statistical details of experiment runs

Run	Actual Value	Predicted Value	Residual	Student Residual	Outlier t
1	4.66	4.56	0.10	0.157	0.149

2	5.80	5.19	0.61	1.080	1.090
3	3.99	3.40	0.59	0.943	0.937
4	4.02	4.32	-0.30	-0.883	-0.873
5	14.63	13.47	1.16	2.282	3.126
6	4.10	3.64	0.46	0.786	0.770
7	7.03	6.45	0.58	2.217	2.949
8	5.18	5.71	-0.53	-1.033	-1.037
9	8.63	9.46	-0.83	-1.841	-2.149
10	3.77	3.55	0.22	0.582	0.562
11	2.61	2.73	-0.12	-0.237	-0.225
12	11.00	10.09	0.91	1.500	1.617
13	7.76	8.38	-0.62	-1.096	-1.108
14	5.31	5.77	-0.46	-0.979	-0.977
15	5.04	5.60	-0.56	-0.940	-0.934
16	14.55	15.13	-0.58	-2.217	-2.949
17	6.74	7.11	-0.37	-0.531	-0.511
18	7.12	7.11	0.01	0.016	0.015
19	6.83	7.11	-0.28	-0.401	-0.384
20	7.13	7.11	0.02	0.031	0.030

After the model is determined to be appropriate, the response equation can be determined and plotted. The Design Expert quadratic model is shown in Table 5 and Figure 44 below. In addition, the relative effect of each factor and factor combination is determined. This is done by normalizing the response equation coefficients based on the range of each factor, and then determining the relative effect of each normalized coefficient on the TCE ratio. This plot indicates that the TCE ratio is dependent on all three factors because and is shown in Figure 45.

Table 5: Design Expert regression parameters

C0	20.87		
C1	-31.602	x	Spacing
C2	2,680.5	y	Strand Area

C3	-24.57
C4	4.6077
C5	-18,204
C6	12.061
C7	-110.76
C8	22.111
C9	-2,327

z	Open Space
x²	Spacing ²
y²	Strand Area ²
z²	Open Space ²
x*y	Spacing*Strand Area
x*z	Spacing*Open Space
y*z	Strand Area*Open Space

$$TCE = C0 - C1*x + C2*y + C3*z + C4*x^2 + C5*y^2 + C6*z^2 + C7*x*y + C8*x*z + C9*y*z$$

Figure 44: The TCE ratio prediction equation developed in this experiment

Figure 45: The contribution of the factors to the TCE ratio prediction equation

The surface predicted by this equation exists in 4-dimensional space (1 dependent variable and 3 independent variables); therefore the creation of a simple, easy-to-read, plot is difficult. By holding one factor constant, 3 separate plots can be generated to represent the 4-dimensional space. The response surface for this experiment can be seen in [Figure 46](#), [Figure 47](#), and [Figure 48](#). As has been previously stated, the optimal TCE ratio for a PCM storage system that is currently under consideration is approximately 4x.

Model:
 Quadratic
 Response:
 TCE
 Actual variables:
 X = Spacing
 Y = Strand Area
 Actual constants:
 Open Space = 0.7400

Figure 46: A plot of the prediction equation showing the TCE ratio relationship to spacing and strand area. Open space is held constant at 74%.

Model:
Quadratic

Response:
TCE

Actual variables:
X = Spacing
Y = Open Space

Actual constants:
Strand Area = 2.16E-02

Figure 47: A plot of the prediction equation showing the TCE ratio relationship to spacing and open space. Area is held constant at .0216 in².

Model:
Quadratic

Response:
TCE

Actual variables:
X = Strand Area
Y = Open Space

Actual constants:
Spacing = 1.286

Figure 48: A plot of the prediction equation showing the TCE ratio relationship to strand area and open space. Spacing is held constant at 1.286 in.

Although this experiment has been designed to predict TCE ratio based on the three independent factors, the TCE can be reduced to functional relationship with only a single independent variable. This independent variable effectively combines all 3 factors into a single variable called the void fraction.

The void fraction (VF) simply describes the volumetric fraction of the total test article that is not occupied by TCE. In this experiment, the void fraction can be described as a moderately-accurate predictor of the TCE ratio in the samples. The relative inaccuracy of this model is partially the result of error introduced by measuring the void fraction, which is described in Section 0. The relationship between the TCE ratio and VF determined in this experiment should not be used to predict the TCE ratio when different shapes of TCE material are used. This is because the correlation is dependent on the overall shape of the TCE (i.e. the diamond pattern dimensions). To accurately view this correlation, the TCE ratio versus VF has been plotted as separate data sets for .75" expanded metal enhanced specimens and the test articles with 1.5" TCE embedded, as shown in **Figure 49**. However, **Figure 50** does indicate a good linear relationship between VF and TCE ratio for the combined data set, despite the fact that 2 different expanded metal shapes are used. While this plot maybe a sufficient correlation for these 2 sizes, it's not certain that expanded metals of a much larger or much smaller diamond pattern would be accurately represented along with the tested shapes. **Figure 50** summarizes the correlation between void fraction and TCE ratio, and can be described as a less accurate method of predicting the response variable compared to the 3-factor model described previously. The model does have the advantage, however, of being parameterized by only the void fraction, which is relatively easy to measure.

Figure 49: The relationship between the TCE ratio and void fraction with each type of expanded metal separated. Error bars are based on measurement uncertainty in TCE ratio (See Section 0)

Figure 50: The relationship between the TCE ratio and void fraction with data from both typed of expanded metals combined. Error bars are based on measurement uncertainty in TCE ratio (See Section 0)

Uncertainty Analysis

The uncertainty in the results of this experiment is dependent on the uncertainty in experimental measurements and the uncertainty in the repeatability of the experimental results. The overall uncertainty of the experimental results will be important in future applications of this experiment.

The measurement uncertainty of this experiment is derived from the propagation of any uncertainty in the measured variables. The uncertainties in the thermal conductivity and the TCE ratio are investigated. The equation used to calculate the thermal conductivity, k , can be seen in **Figure 51**. In this equation, V is the volts supplied to the heater, I is the amps supplied to the heater, L is the distance (m) between the thermocouple probes used to find the temperature difference, A is the cross-sectional area (m²) of the test article, and ΔT is the temperature difference (K or °C) across the section of test article that was analyzed. In addition, the previously-mentioned TCE ratio is shown in **Figure 52**.

$$k = \frac{V \times I \times L}{A \times \Delta T}$$

Figure 51: The relationship of the thermal conductivity to the measured variables in this experiment

$$TCE = \frac{k_{test\ article}}{k_{plain\ wax}}$$

Figure 52: The TCE ratio relationship

As can be seen in **Figure 51**, the thermal conductivity depends on five measured variables. To determine the uncertainty for each measured the uncertainty in the area measurement and the temperature measurement must first be calculated. This is because the uncertainty in these measurements is dependent on other measured variables. For example, the area calculation is based on the measured diameter, d , of the test article. The uncertainty in the diameter measurement is assumed to be $\pm .0625$ inches (± 0.0015875 m). In addition, the temperature difference is dependent on the uncertainty in each of the thermocouple measurements used to calculate it. The uncertainty in each thermocouple measurement is assumed to be $\pm .3^\circ\text{C}$, based on a detailed analysis of the thermocouples and data acquisition system [1]. The uncertainty calculations for ΔT and A have been carried out according to the equations in **Figure 53** and **Figure 54** with the aid of the Engineering Equation Solver (EES). **Table 6** is completed based on these results.

$$\sigma_A = \sqrt{\left(\frac{\delta A}{\delta d}\right)^2 (\sigma_d)^2}$$

Figure 53: The calculation of uncertainty of the test article area term

$$\sigma_{\Delta T} = \sqrt{\left(\frac{\delta(\Delta T)}{\delta T_1}\right)^2 (\sigma_{T_1})^2 + \left(\frac{\delta(\Delta T)}{\delta T_2}\right)^2 (\sigma_{T_2})^2}$$

Figure 54: The calculation uncertainty in the temperature difference between the thermocouple probes

Table 6: A summary of the uncertainty for each variable that governs the thermal conductivity of each test article

Variable	Uncertainty (relative or absolute)
V	.1% of reading + 1 LSD
I	.6% of reading
L	.0625 in (0.001588 m)
A	.1963 in ² (0.0001267 m ²)
ΔT	.4243 K or °C

Based on the uncertainties shown in Table 6, the total uncertainty in the thermal conductivity and the TCE ratio due to measurements can be calculated based on the equations seen in Figure 55 and Figure 56. Note that average experimental value of each variable has been used in all calculations. The total uncertainty in the thermal conductivity due to measurements made in this experiment is determined to be $\pm .176$ W/(m*K). The uncertainty in the thermal conductivity of the plain wax specimen is calculated separately as $\pm .02772$ W/(m*K), based on the experimental values of the plain wax test. Based on this uncertainty and the uncertainty of the thermal conductivity of the average test article with TCE, the uncertainty due to measurement of the TCE ratio is determined as $\pm .4407$.

$$\sigma_k = \sqrt{\left(\frac{\delta k}{\delta V}\right)^2 (\sigma_V)^2 + \left(\frac{\delta k}{\delta I}\right)^2 (\sigma_I)^2 + \left(\frac{\delta k}{\delta L}\right)^2 (\sigma_L)^2 + \left(\frac{\delta k}{\delta A}\right)^2 (\sigma_A)^2 + \left(\frac{\delta k}{\delta T}\right)^2 (\sigma_T)^2}$$

Figure 55: The calculation of uncertainty for the thermal conductivity

$$\sigma_{TCE} = \sqrt{\left(\frac{\delta TCE}{\delta k_{plain\ wax}}\right)^2 (\sigma_{k_{plain\ wax}})^2 + \left(\frac{\delta TCE}{\delta k_{test\ article}}\right)^2 (\sigma_{k_{test\ article}})^2}$$

Figure 56: The calculation of uncertainty for the TCE ratio

The uncertainty in the repeatability of this experiment is estimated using the four redundant tests that were carried out on test articles with the same design configuration. To do this, the thermal conductivity value of the mean of these repeat tests is estimated using a t-distribution with 3 degrees of freedom. By using a 95% confidence level, the mean of these data points is estimated to be accurate within $\pm .177$ W/m*K. This can be described as the random error component of the uncertainty for this experiment. This value is not estimated for the plain wax specimen because thorough repeat tests have not been carried out on plain wax test articles. It can be estimated, however, that the repeatability uncertainty of plain wax test articles would be less than that of the average test article with TCE. This is because a plain wax test article has less experimental variability due to the simplified manufacturing process.

The total uncertainty in the measured thermal conductivity has been calculated, based on the equation in Figure 57. The total uncertainty of the TCE ratio cannot be accurately

estimated because the uncertainty due to repeatability is unknown. A summary of the calculated uncertainties can be seen in Table 7. Note that these values are based on averaged experimental results.

$$\sigma_{total} = \sqrt{(\sigma_{measurement})^2 + (\sigma_{repeatability})^2}$$

Figure 57: The calculation of the total uncertainty

Table 7: A summary of the uncertainties in this experiment

	Thermal Conductivity	TCE Ratio
Average Value	3.495 W/(m*K)	6.241
Measurement Uncertainty (absolute)	.176 W/(m*K) (average)	.4407 (average)
Measurement Uncertainty (relative)	5.04%	7.06%
Repeatability Uncertainty (absolute)	.177 W/(m*K) (average)	Unknown
Repeatability Uncertainty (relative)	5.06%	Unknown
Total Uncertainty (absolute)	.250 W/(m*K) (average)	Unknown
Total Uncertainty (relative)	7.15%	Unknown

Error Analysis of Experiment

As is evident in the presented results, both systematic and random error is present in this experiment.

One likely source of systematic error is the inability to ensure that every sheet of TCE was in direct contact with the aluminum cylinder when properly spaced. A small gap between the TCE and the aluminum cylinder existed in many runs because of the difficulty resulting from cutting the TCE sheets to exact specifications. This error is not easily quantifiable; however, it can be estimated to be small because the percentage amount of TCE that was excluded is small.

Another source of potential systematic error is the discrepancy between the manufacturer-specified strand area and the actual sample strand area. The manufacturer values have been assumed to be an accurate and exact dimensional representation actual expanded metal used in the experiment. The strand area has not been directly measured, however through simple calculations the strand area has been estimated based on the void fraction of each sample. A summary of the differences between estimated strand areas vs. the manufacturer's specified strand area is summarized in Table 8. A relatively low correlation does appear to exist between the percent difference between the manufacturer-specified dimensions and calculated strand area versus the absolute value of the studentized residuals between the TCE ratio predicted by the Design Expert model developed previously and experimentally-observed TCE ratio. This correlation can be seen in Figure 58. The correlation is low ($R^2=.1527$).

Table 8: The difference between the manufacturer-specified strand area and the experimentally-observed strand area

Run	Manufacturer States Strand Area (in ²)	Calculated Estimate of Strand Area (in ²)	Percent Difference
1	0.0104	0.0108	-3.9110
2	0.0134	0.0092	45.8125
3	0.0056	0.0059	-4.6162
4	0.0204	0.0184	10.6290
5	0.0213	0.0219	-2.9421
6	0.0104	0.0099	4.2149
7	0.0376	0.0304	23.7441
8	0.0213	0.0214	-0.6723
9	0.0134	0.0112	19.3464
10	0.0134	0.0115	15.9124
11	0.0056	0.0052	7.7069
12	0.0204	0.0198	2.8434
13	0.0213	0.0198	7.5410
14	0.0056	0.0056	0.4052
15	0.0104	0.0096	8.1916
16	0.0376	0.0312	20.4095
17	0.0204	0.0196	4.0185
18	0.0204	0.0208	-2.0113
19	0.0204	0.0206	-1.0624
20	0.0204	0.0209	-2.6171

Figure 58: The slight trend between observed strand area difference and the absolute value of the studentized residual between observed TCE ratio and TCE ratio predicted by Design Expert model

Another potential systematic error in this experiment is the introduction of voids (air pockets) into the test articles. These voids occur when the wax cools and shrinks from the TCE and/or collapses on itself forming hollow spaces within the molded specimen. These voids lower the overall thermal conductivity of the test article as the air pockets act as an additional thermal resistance. A qualitative assessment of the overall condition (including voids and depressions in the wax) of the test articles has been carried out. Based on this assessment, no significant correlation exists between overall test article condition and the residuals between the TCE ratios predicted by the Design Expert model and experimental TCE ratios. The qualitative assessment may not be a good indication of the amount of voids that exists on the interior of each test article.

Finally, the heat loss associated with this experiment is likely a systematic error present and could be quantified with more experimentation. Heat loss through the thermocouple wires has been physically observed, which may have an effect on the observed temperature gradient in the sample. Most of this heat loss likely occurs between the heater and the TC probes within the aluminum puck, through the bottom insulation, the skins of the cylindrical wall and through the seam where the insulation is taped together.

Most of the random errors present in this experiment are likely the result of experimental error encountered during the construction and testing of the test articles. These errors may include observation errors that result from reading scales, calipers, etc. In addition, some

environmental error may be present in form of fluctuations in room temperature between the tests and instabilities in the voltage supplied to the heater. In addition, various edge effects, due to cut strands that do not form a complete path, may also have contributed to the error in the experiment.

Several plots of the standard error, which describes the accuracy of fit of the quadratic regression, are shown in **Standard Error Plots**. The standard error calculated using Design Expert.

Analytical Model Results

In addition to the model that was determined experimentally, a simple analytical, heat transfer model was developed to predict the TCE ratio of the test articles. The model is based on 1-dimensional, conductive heat transfer through parallel resistance paths. The model can be describes as a moderate to low accuracy predictor for the TCE ratio based on the experimental variables, however, the purpose of this model is to verify the relative accuracy of the experiment. Further development of this model may enhance its' accuracy.

To develop this model, the void fraction and height of each test article has been measured. From this information, the cross-sectional area of aluminum TCE in the test article can be determined. Additionally, the length of the continuous paths in the aluminum TCE is measured using a caliper. As previously stated, the long axis of the diamond pattern has been oriented vertically. The thermal resistance, R_{Th} , can be determined for the parallel conduction paths through the wax and aluminum. As can be seen in Figure 59, R_{th} depends on the path length, L , the thermal conductivity of the material (known for wax and aluminum), k , and the cross-sectional area, A . The equivalent resistance network used in this model can be seen in Figure 60.

$$R_{Th} = \frac{L}{k \times A}$$

Figure 59: The equation for thermal resistance used for the analytical model

Figure 60: The equivalent thermal resistance network used in this model

Using the thermal resistance network in Figure 60, a single, equivalent thermal resistance of the test article can be calculated. When this has been determined, the equation seen in

Figure 59 can be used to determine the bulk thermal conductivity of the test article (by solving for k).

Error Analysis of Analytical Model

During this experiment, the analytical model has been used to loosely verify the results reached experimentally. The difference between the thermal conductivity found experimentally and that found analytically is sometimes large. A summary of the differences can be seen in Table 9. A graphical comparison can be seen in Figure 61.

Table 9: A summary of the error between the experimentally-determined values and the TCE ratio values predicted by the analytical model

Run	Experimental Thermal Conductivity (W/m*K)	Analytical Model Prediction (W/m*K)	Percent Difference (%)
1	2.607	2.507	-3.838
2	3.249	2.540	-21.838
3	2.233	1.575	-29.476
4	2.252	2.602	15.568
5	8.191	7.984	-2.519
6	2.293	2.130	-7.138
7	3.934	5.150	30.899
8	2.898	3.846	32.714
9	4.832	4.466	-7.572
10	2.110	2.322	10.016

11	1.459	1.301	-10.856
12	6.160	5.858	-4.906
13	4.348	4.862	11.842
14	2.975	2.393	-19.555
15	2.825	2.909	2.977
16	8.149	9.320	14.371
17	3.776	4.020	6.460
18	3.988	4.253	6.667
19	3.826	4.222	10.329
20	3.994	4.313	7.990

Figure 61: A comparison between the experimental TCE ratio and the TCE ratio predicted by the analytical model

As can be seen in Table 9, the percent difference is as large as ~30% in some cases, however the analytical results are not substantially biased higher or lower than the experimental value. The error appears to be most strongly correlated with the strand area of the sample, as illustrated in Figure 64. Several potential reasons exist for the error between the analytical model results and the experimental values. The first reason is the error that is introduced when measuring the void fraction of the material. This was done by measuring the length and weight of the metal as it was placed in the test article. This metal extended out of the top of the test article until the top portion of the test article was removed with a saw. The height of the sawed test article was then measured, and the volume of TCE in the test article was estimated. Photos of a test article before and after the top section was sawed

off are shown in **Figure 62**. The error associated with this process may explain much of the difference seen between the analytical model results and the experimental results.

Figure 62: A test article before (left) and after (right) the top has been sawed off. Note that the TCE material in the right photo is not expanded metal and was not used in this experiment.

Additional variation in the difference between the analytical model and the experimental results may be caused by the effect of “dangling” strands. The incomplete strands are sometimes created when manufacturing the test articles. The strands are trimmed to fit and an integer number of strands is not always the best fit. The heat transfer through the trimmed strands is much more complex and is not accounted for in the analytical model. An example of a “dangling” strand is shown in **Figure 63**.

Figure 63: A section of expanded metal showing partial “dangling” strands at the top

A potential correlation has also been observed between the percent deviation of the analytical model TCE ratio results (from the experimental results) and the strand area of the TCE material (as specified by the manufacturer). A summary of this correlation can be seen in **Figure 64**. One possible explanation could be the increased effect of “dangling” strands in test articles with heavier expanded metal. These test specimens usually have fewer sheets of TCE, which causes the “dangling” strands to make up a higher percentage of these test articles. The larger percentage of dangling strands increases the relative effect of these features. In addition, test articles with larger strand area may have higher error due to edge effects. Edge effects occur at areas, usually near sharp edges (i.e. where a TCE sheet has been cut), that have unpredictable heat transfer. In test articles with large strand areas, the length of the edges at a cut location is larger. Due to the unpredictable effects at these edges, the contribution of these edge effects may be larger in test articles with heavy strands.

Figure 64: The relationship between strand area and the percent difference between the experimental results and the analytical model results

SolidWorks Simulation Results

In addition to the experimental and analytical models developed during this project, the accuracy of computer thermal simulations has been investigated. To perform this analysis, an FEA simulation has been completed in SolidWorks 2010-2011. The results of this computer simulation are useful in verifying the overall accuracy of the experiment and for general comparison purposes. One very important conclusion observed from the SolidWorks simulation is that the temperature gradient in the interior of the test article is reasonably uniform across a horizontal cross-section. As can be seen in Figure 65, the temperature profile appears to vary linearly with height and the temperature seems uniform across each horizontal cross-sectional slice. Some variability of the temperature gradient has been observed near the edges of some test articles, however, near the center of the test articles (where the thermocouples are located during testing), the temperature gradient appears linear.

Figure 65: The temperature gradient of a test article. Note that the temperature appears uniform at horizontal cross sections.

The computer simulation has been set up by first applying a temperature of 40°C to the bottom of the test article and 0°C to the top. Then an adiabatic boundary condition is applied to exterior surfaces, including the outside cylinder face and the side and bottom of the heater puck. Contact resistances between the expanded metal and the wax and at the wax/aluminum puck interfaces are neglected. At this point, the FEA simulation is run and the average heat flux, in W/m^2 , is then determined. From this information, the average power required to create this temperature difference can be calculated based on the cross-sectional area of the model. The power indicated by the SolidWorks model can then be compared to the power required in the experimental runs. A plot showing the FEA mesh and an exploded view of the modeled components can be seen in Figure 66.

Figure 66: An expanded view of a test article with the FEA mesh shown

The SolidWorks simulation results further enforces the validity of this experiment, as it predicts reasonable values near those observed in the experiment. The results of the computer simulations can be seen in **Table 10**. Note that the void fraction has been calculated for each of the SolidWorks runs. A plot of the power input as a function of void fraction from the experimental data and the computer simulations are shown in **Figure 67**. As can be observed, the power predictions in the SolidWorks simulations are less than that required in the experiment. The difference between the two data sets can also be described as somewhat constant. This relatively-constant offset can be estimated as .69 W, based on the power difference of the plain wax computer model and plain wax experimental data. Heat loss is determined to be the highest contributing factor to the power difference between the computer models and the experiment test articles.

Overall, the test data validated the accuracy of the simulation results giving us confidence in the ability to use a tool such as SolidWorks and its' simulation package to predict accurately the performance of a TCE. While more detailed CAD models and simulations should be investigated to give more accurate results, this initial investigation opens up opportunities for exploring other TCE options and saving significant time through the use of finite element, thermal simulations.

Table 10: The computer simulation results

Exp. Run	Material Description	Experimental Void Fraction	SolidWorks Void Fraction	Experimental Power	SolidWorks Power	Percent Difference
1	1 1/2 .081 R AL 3003H14	0.9856	0.9808	3.23	2.42	-24.93
2	3/4 .081H R AL 3003H14	0.9841	0.973	4.2	3.36	-20.11
3	1 1/2 .051 R AL 3003H14	0.9918	0.9898	3.16	2.18	-30.95
4	1 1/2 .125 R AL 3003H14	0.9844	0.9811	3.19	2.70	-15.45
5	3/4 .125 R AL 3003H14	0.9454	0.9248	8.08	8.36	3.45
6	1 1/2 .081 R AL 3003H14	0.9884	0.9856	3.31	2.55	-23.10
7	3/4 .188 R AL 3003H14	0.9630	0.9433	5.75	7.50	30.36
8	3/4 .125 R AL 3003H14	0.9744	0.9698	4.76	4.74	-0.33
9	3/4 .081H R AL 3003H14	0.9692	0.9542	6.59	5.37	-18.50
10	3/4 .081H R AL 3003H14	0.9861	0.9815	3.62	2.77	-23.46
11	1 1/2 .051 R AL 3003H14	0.9942	0.9921	2.75	1.87	-32.02
12	1 1/2 .125 R AL 3003H14	0.9599	0.9456	6.688	6.24	-6.64
13	3/4 .125 R AL 3003H14	0.9660	0.9556	6.05	4.98	-17.61
14	1 1/2 .051 R AL 3003H14	0.9856	0.9821	4.29	2.81	-34.54
15	1 1/2 .081 R AL 3003H14	0.9822	0.9763	3.82	2.35	-38.42
16	3/4 .188 R AL 3003H14	0.9295	0.885	8.01	9.55	19.24
17	1 1/2 .125 R AL 3003H14	0.9734	0.9638	5.24	4.60	-12.23
18	1 1/2 .125 R AL 3003H14	0.9719	0.9638	5.75	4.60	-20.01
19	1 1/2 .125 R AL 3003H14	0.9722	0.9638	5.02	4.60	-8.38
20	1 1/2 .125 R AL 3003H14	0.9719	0.9638	5	4.60	-8.01
N/A	Plain Wax	1.0000	1.0000	1.754	1.066	-39.22

Figure 67: The correlation between power and void fraction between the experimental and computer results. Note the difference in the power for a sample having a void fraction of 1 (plain wax). This discrepancy in the modeled vs. experimental power can be attributed to the adiabatic model vs. the actual heat losses in the experiment.

Error Analysis of the SolidWorks Model

The variability in the computer simulation data may be mostly attributed to the method with which the computer models have been constructed. The expanded metal sheets have been placed in the wax material such that the sheets are evenly spaced between the sides of the aluminum cylinder. Care has not been taken to align the sheets within the wax such that the highest number of complete paths of aluminum is present. This effect can be seen in Figure 68; note that partial strands occur on both sides of the sheet. Through optimization, the number of partial strands could be reduced. In the experiment, the sheets have been trimmed to maximize the number of continuous paths and minimize the amount of partial paths consisting of “dangling” pieces that have had the ends trimmed. The computer model has not been optimized in this fashion and could be subject to some inconsistency due to this fact. A study to determine the variation in power could be explored in the future to quantify this variability.

Figure 68: An example of an expanded metal sheet used in a SolidWorks model. Note that partial strands exist on both sides of the sheet. Optimization would decrease the number of partial strands by moving the location of the cut section.

A major reason that the SolidWorks Simulation results differ from the experimental results is the adiabatic condition that constrains the surfaces of the computer model surfaces where heat loss may be occurring in the experiment. This likely explains the offset that appears apparent between the power required to maintain the temperature difference of 40°C in the computer model versus the power required in the experiment. This difference is one indication that considerable heat loss is occurring in the experimental setup.

Conclusion

Summary and Discussion of Results

This experiment has been designed to determine the effects that expanded metal TCE will have on the bulk thermal conductivity of a substrate material. The experiment is specifically intended to determine material requirements to achieve a TCE ratio of approximately 4x,

which is required to optimize the current PCM systems under investigation. The results of this experiment clearly demonstrate that a thermal conductivity enhancement of 4x is possible while keeping the volume and cost of TCE material to a manageable level. For example, approximately 99% of the storage volume of a LHSS may be composed of the storage material, with only 1% of the volume occupied by TCE.

The Design Expert model regression fit the experimental with minimal errors and may be used to accurately predict the TCE ratio of a composite test sample using expanded metals similar to those in this project. It should be noted that the prediction equation shows an increase in standard error as the strand area is increased as seen in **Figure 69**. The model shows low standard error when the TCE ratio is near the optimum value of 4x. For these reasons, the prediction equation developed in this experiment should be considered most accurate at lower (3-8x) TCE ratio values. In addition, the uncertainty of the measurement taken in this experiment should be considered. The uncertainty due to measurements of the TCE ratio is estimated as 7.06%.

Also, the absolute value of the residual between the regressed TCE ratio model fit and the experimental TCE ratios show an increasing trend as the experimental TCE ratio increases in value. This can be seen in **Figure 70**.

Model:

Quadratic

Response:

SE mean

Actual variables:

X = Spacing

Y = Strand Area

Actual constants:

Open Space = 0.7400

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Figure 69: The standard error as a function of spacing and strand area. The units of Spacing are inches, the units of Strand Area is inches², the units of Standard Error is TCE ratio

Figure 70: The slight upward trend of the studentized residual as TCE ratio is increased

To supplement the experimental results, an analytical model and a computer simulation have been developed to predict the TCE ratio of the test articles used in the experiment.

The analytical model has been established using a thermal resistance network simplification and with the assumption of simple 1-dimensional, conductive heat transfer. This model fits the experimental data loosely, with the error resulting from both experimental variability and over-simplification of the analytical model. The analytical model serves the purpose of roughly verifying the results of the experiment, and further development may be desired to increase accuracy further.

The computer model has been created using SolidWorks. Each test article manufactured during the experiment has been modeled with SolidWorks and the simulation has been run to compare the experimental results with a CAD/FEA solver. The comparison has determined that computer simulations closely result in the same heat fluxes collected in the experiment. Due to the simplification of the FEA model using adiabatic surfaces, an offset in the comparison is most likely attributable to the heat loss experienced in the actual experiment.

Outlier Discussion

After analysis of the experimental data, it is clear that experimental test articles that exhibited high thermal conductivity and/or contained a TCE material with a large strand area displayed increased outlier effects. This is evidenced by the increasing experimental residuals at high thermal conductivity values and the increasing standard error associated with the Design Expert regression at large strand areas. These data points deviate from the regression model because of the sparse number of experimental configurations in this region of the experimental design.

Additionally, the test specimens that exhibited high composite thermal conductivities were more responsive to small variation in the source/sink temperatures. This may have contributed to larger experimental error if the ice bath was not well-mixed with the bubbler, allowing the temperature to deviate slightly from 0°C. No reasons exist to discount this data completely; however, some additional testing in the high-conductivity portion of the response space may be desired.

The experimental matrix has been designed to be most accurate at TCE ratios of around 4x. Because of this, tests using the heavier material that resulted in high TCE ratios were less-accurately regressed by the model due to the limited number of experimental configuration in this region of the design space. By adding more test configurations we could decrease the standard error by reducing the outliers and map the results in this region more explicitly.

Physical Significance of Results

This experiment has led to development of a quadratic regression that predicts the TCE ratio based on expanded metal as a means of enhancing the thermal conductivity in wax. Wax has been chosen as the substrate material because it has similar thermal properties to salts used in LHSS designed for concentrating solar power applications. An assumption has been made that the TCE ratio seen in a wax composite samples using expanded metal will be similar to the enhancement that will be seen in a PCM system employing salt. Future experimentation will be required to assess the validity of this assumption. If this assumption is valid, the experimental results will be used to determine the geometry and quantity of expanded metal required to achieve the desired thermal conductivity.

In addition to the quadratic regression based on three factors, a prediction equation based only on void fraction has been established. This regression may be used to predict the TCE ratio of test articles that use similar TCE to that used in this experiment. The single factor model should be considered less accurate overall compared to the three-factor model because of error introduced when estimating the void fraction.

Future Extensions of Experiment

The models developed during this experiment should be considered accurate for expanded metals with properties and factors that are similar to the samples used in these tests. Future experimentation or computer simulations may focus on developing TCE prediction models for materials that are shaped differently or have different properties.

Further experimentation may also be required to confirm the validity of the results observed in this experiment and to assess the scalability of these results. One major systematic source of error in this experiment that may need to be more closely analyzed is the heat loss through the experimental setup. During the experiment, heat has been lost through the insulation skin, insulation seam, the bottom insulation as well as through the thermocouple wires which are inserted into the test article. The computer simulations run during this experiment estimate the total heat loss at approximately 0.69 W total heat loss, however further experimentation or analysis may be required to determine a more accurate heat loss value. It should be noted that by using TCE as the response variable, defined as the factor increase in thermal conductivity, the bias error due to heat loss present in this

experiment has been normalized and should have a minimal effect on the TCE ratios in this experiment.

The scalability of this experiment is of importance because of the large difference between the experimental setup and the LHSS tanks to which expanded metal TCE material may be applied. The most effective method to analyze the scalability of these results is to perform larger-scale experiments. The "fish tank" experiment, which is currently being developed as a medium-scale PCM experiment, will yield results on the scalability of the TCE ratios presented in this report. Additional experiments at a larger size will be important in verifying the scalability of these experimental results.

Acronyms

CSP – Concentrated Solar Power
EES – Engineering Equation Solver
FEA – Finite Element Analysis
HTF – Heat Transfer Fluid
HX – Heat Exchanger
LHSS – Latent Heat Storage System
PCM – Phase Change Material
TC – Thermocouple
TCE – Thermal Conductivity Enhancement
TES – Thermal Energy Storage
VF – Void Fraction

References

Jon Paul, 2004, "Natural Convection Loops Providing Overheat Protection in Flat-Plate Collector and Integral-Collector Storage Solar Water Heating Systems," Ph.D. Thesis, Department of Civil, Environmental, and Architectural Engineering, University of Colorado, pp. 308.

Appendix F-1 – Experimental Procedure

Materials and Equipment

- 1.) Paraffin Wax Slab, melt temperature 133-135 °F.
- 2.) At least one 4" ID aluminum thin-wall tube 6" length.
- 3.) At least one 4" OD aluminum puck approximately .5" height, with three holes drilled .5" deep on OD surface of puck. Holes drilled horizontally .5" deep toward center of puck. Holes must be large enough to accommodate a thermocouple.
- 4.) At least one adhesive AC heater, applied to bottom surface of aluminum puck.
- 5.) Expanded metal TCE.
- 6.) Adequate insulation. 4" ID 1.5" thick pipe insulation is used on outside of test article. 4" diameter 4" tall insulation plug is used on bottom surface.
- 7.) Eight thermocouple probes and a data acquisition/logging system (Campbell CR1000 used)
- 8.) Bubbler to agitate ice bath.
- 9.) Two multi-meters.
- 10.) At least one Variac AC voltage controller.
- 11.) Mold release spray.
- 12.) Double boiler or similar wax-melting apparatus.
- 13.) Electrical tape.
- 14.) Sealant (silicone-type or similar)
- 15.) Ice and water.

Test Article Construction Procedure

The construction of each test article is performed in several steps. Care is taken during each step to ensure that the test article is free of defects that may introduce experimental error. The construction process can be summarized by the following steps:

- 1.) Heat wax until melted in a double boiler or similar apparatus (See **Figure 71**).
- 2.) Clean top surface of aluminum puck to remove oxidation layer and spray inside surface of aluminum tube with mold release spray.

- 3.) Insert aluminum puck into aluminum tube until bottom of puck (with heater) is parallel with end of tube. Seal puck-tube interface with tape if necessary.
- 4.) Place puck and tube combination on flat surface with open side of tube facing up.
- 5.) Cut and insert TCE into open end of tube so that the bottom edge of each sheet of TCE contacts the puck and each of each sheet contacts the inside of the aluminum tube when the sheets are evenly spaced. The TCE may extend above the top of the tube as it will be cut later.
- 6.) Fix the TCE sheets in place (clamps and wood blocks are used in this experiment).
- 7.) Pour the melted wax into the open end of the tube approximately 1" deep. Let cool (2-3 hours) and repeat the pouring process by 1" each pour until the tube is near full. Multiple pour decreases chances of voids occurring as wax cools and shrinks (See Figure 71).

Figure 71: A double boiler used to melt the wax (left) and pouring the wax into the test article cylinder (right)

- 8.) After all wax has cooled, remove aluminum tube from wax by sliding upward.
- 9.) Cut the top of the wax and TCE to leave approximately 4.75" of wax left on top of the puck.
- 10.) Drill 4 holes into the wax cylinder starting 1" from top of puck and then every 1". The holes should be 2" deep and large enough to accommodate a thermocouple (See Figure 72).
- 11.) The puck is adhered only to the wax, so care must be taken to ensure it does not become dislodged.

12.) Use sealant to fix the aluminum tube to the approximately the top .5" of wax, so that the top probe hole is not blocked. This will hold an ice bath on top of the wax and must be water-tight. A completed test article is shown in **Figure 72**.

Figure 72: A test article that has had the top sawed off and the probe holes drilled (left) and a test article with the aluminum cylinder fixed on top, ready for testing (right). Note the TCE in the pictured test articles is not expanded metal and was not used in this experiment.

Testing Procedure

The test article is assessed to determine the thermal conductivity using the following procedure:

- 1.) Insert thermocouple probes into the three drilled holes in the puck, the four drilled holes in the wax, and one probe in the top ice bath area contacting the wax surface. Thermally conductive grease or lubricant may be added to increase accuracy of thermocouple measurements. (See **Figure 73**)
- 2.) Insulate the test article on the bottom and sides using pipe insulation or similar, allowing thermocouple and heater wires to protrude.
- 3.) Insert ice and water into the top cylinder to form a small reservoir. Insert a bubbler or agitator into the ice bath. The ice bath of a test article can be seen in **Figure 73**.

Figure 73: A test article with thermocouple probes inserted (left) and a test article with insulation ready to be taped closed (right)

- 4.) Set up the multi-meters to monitor AC voltage and current supplied to the heater. Plug the heater into the AC Variac.
- 5.) Supply heat to the system and maintain ice in the ice bath. The test setup can be seen in **Figure 74**.

Figure 74: The testing setup used in this experiment

- 6.) Monitor the thermocouple temperatures and slowly allow the system to reach steady state (2-6 hours). Adjust the voltage so that steady state occurs with the puck temperature near 40 °C and the ice bath as close to 0 °C as possible. The probes along the length of the ice bath will show a temperature gradient in the wax.
- 7.) Use the equation shown in **Figure 75** to determine the thermal conductivity, k (W/m*K). In this equation, q is the AC power (W) supplied to the heater, L is this distance (m) between two of the probes in the wax (use the furthest spaced for most accuracy), A is the area (m²) of the circular cross-section of the wax test article, and ΔT is the temperature difference (°C or K) between the two selected probes. Use this k -value to find the TCE. It has been determined experimentally that the thermal conductivity of the plain wax used in this experiment is .56 W/m*K.

$$k = \frac{q \times L}{A \times \Delta T}$$

Figure 75: The equation used to calculate thermal conductivity

Appendix F-2 – Plot and Figures

Standard Error Plots

Model:
Quadratic

Response:
SE mean

Actual variables:
X = Spacing
Y = Strand Area

Actual constants:
Open Space = 0.7400

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Figure 76: A plot of standard error with the independent variables of spacing and strand area. Open space is set constant at .74. Note that standard error increases as strand area is increased and does not appear dependent on spacing.

Model:
Quadratic

Response:
SE mean

Actual variables:
X = Spacing
Y = Open Space

Actual constants:
Strand Area = 2.16E-02

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Figure 77: A plot of the standard error with the independent variables of spacing and open space. Strand area is set constant at .0216 in².

Model:
Quadratic

Response:
SE mean

Actual variables:
X = Strand Area
Y = Open Space

Actual constants:
Spacing = 1.286

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Figure 78: A plot of the standard error with the independent variables of strand area and open space. Spacing is set constant at 1.286 in.

Appendix G – ORNL corrosion report

Power Conversion Material (PCM) and Stainless Steel Corrosion Testing

D. F. Wilson
W. W. Willoughby

June 2013

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Materials Science and Technology Division

Power Conversion Material (PCM) and Stainless Steel Corrosion Testing

D. F. Wilson
A. W. Willoughby

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
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EXECUTIVE SUMMARY

To be written

1.0 INTRODUCTION

1.1 BACKGROUND

This work addresses the corrosion behavior of metallic materials for containment of salts for solar energy applications. Abengoa Solar, Inc., is interested in determining economically viable materials to contain salts of interest. These salts are a ternary chloride salt, MgCl_2 - KCl - NaCl , two binary chloride salts, NaCl - MgCl_2 and CaCl_2 - NaCl , and a ternary carbonate salt, Li_2CO_3 - Na_2CO_3 - K_2CO_3 .

The phase diagram presented in Figure 2 shows that the eutectic temperature of MgCl_2 - KCl - NaCl (34.3 – 40.7 – 25 mol %) is approximately 400 °C.¹ As presented in Figures 3 and 4, the eutectic temperature for NaCl - MgCl_2 (58 – 42 mol %) is approximately ~445 °C² and that for CaCl_2 - NaCl (48 – 52) mol % is approximately 507 °C.³ As shown in Figure 5, the ternary carbonate, Li_2CO_3 - Na_2CO_3 - K_2CO_3 (41.3 – 32.6 – 26.1 mol %) has a eutectic temperature of approximate 390 °C.⁴

Figure 2. Melting point of MgCl_2 - KCl - NaCl (34.3 – 40.7 – 25 mol %) is approximately 400 °C. Ref. 1

Figure 3. The melting point of NaCl-MgCl₂ (58 – 42 mol %) is ~445 °C. Ref. 2

Figure 4. Melting point of CaCl₂ - NaCl (48 – 52) mol % is ~507 °C. Ref. 3

Figure 5. Melting point of K_2CO_3 - Li_2CO_3 - Na_2CO_3 (41.3 – 32.6 – 26.1 mol %) is approximately 390 °C. Ref. 4

Considerations of constructions cost and availability of materials tend to dictate the use of steels of varying alloying content. However, depending on the alloying additions and thermal-mechanical processing, there are significant differences in the performance of various steels at moderate temperatures in molten salt environments. Steels of increasing alloying additions and as a result, increasing cost, were identified for evaluation as potential containment materials. In addition, in an effort to increase heat transfer, and anodized aluminum alloy was evaluated.

2.0 EXPERIMENTAL DETAILS

2.1 SPECIMENS

Specimens, [approximate dimensions 0.158 cm (1/16 inch) thick X 1.27 cm (½ inch) wide X 2.54 cm (1 inch) long with a 0.099 cm (0.039 inch) diameter hole located 0.318 cm (1/8 inch) from the end centered] of certified Al 5052, 304 SS, 310 SS, 316L SS, and 321 SS were order from Metal Samples.⁵ All specimens were stamped with material type and unique specimen number. Seven of the Al 5052 specimen were shipped to DCHN⁶ where they were matte anodized (Microlox-Natural) to thickness of 0.002" (0.005 cm) and returned to ORNL. As received stainless steel specimens (two 304 SS, four 310 SS, five 316L SS, and five 321 SS) were Electron Beam autogenous welded to a depth of approximately one-half specimen thickness. The tarnish at the welded area was removed using a chemical cleaning procedure for removal of corrosion products and a solution that was 10% nitric acid and 1% hydrofluoric acid in water. The specimens were soaked in the solution for approximately 1 minute and then rinsed in running water followed by ethanol and dried.⁷

2.2 SALTS

A ternary chloride salt, MgCl_2 - KCl - NaCl (34.3 – 40.7 – 25) mol % of melting point (T_{mp}) 400 °C; two binary chloride salts, NaCl - MgCl_2 (58 – 42) mol % of T_{mp} ~445 °C and CaCl_2 - NaCl (48 – 52) mol % of T_{mp} ~507 °C; and a ternary carbonate salt, Li_2CO_3 - Na_2CO_3 - K_2CO_3 (41.3 – 32.6 – 26.1) mol % of T_{mp} = ~390 °C; were evaluated. These salt were produced in separate reaction vessels from as-received individual chemicals sourced from Sigma-Aldrich chemicals. The appropriate weights of salts for the chosen eutectic salt compositions were weighed, mixed and added to mullite crucibles. The salts and crucibles were heated overnight at 200 °C under a flowing nitrogen gas purge to remove moisture. The temperature was increased over a 4-h period to 150 °C higher than the eutectic melting point, and maintain at temperature for approximate 4 hours before slowly cooling to room temperature. These salts were maintained under a nitrogen atmosphere except for loading and unloading specimens.

2.3 TEST PROCEDURE

Features of the test system are shown in Figure 6. The test system was composed of sixteen furnaces and associated crucibles, specimen hangers, thermocouples, gas inlets and outlets and exhaust vents, and associated temperature control and monitoring system. Control and monitor was achieved via LabView software⁸ and associated input and output devices. The weighed and

dimensioned specimens, in groups of four, per the test matrix shown in Table 1, were attached to a mullite rod and inserted into the crucible, above the salt level, under flowing nitrogen gas and the system sealed. The mullite rods and thermocouple wells (closed at one-end mullite tubes) were fitted with o-rings and sealed against the feedthroughs on the top flanges, which also were sealed against the mullite reaction vessels with o-rings. The crucibles were brought to the 50 °C above the eutectic temperature and the specimen were then pushed into the particular salt eutectic mixture. It was planned that one specimen would be removed from testing after 48 and 168 hours, two specimens would be removed from testing after 1000 hours. Removal of specimens were performed under flow nitrogen gas.

Figure 6. Composite image of testing facility showing various components including gas inlets and outlets, exhaust, thermocouples, and power and temperature controls.

Table 1. Test matrix of salts and specimens

Salt	Time (h)*	Specimens ID				
		Al 5052	304 SS	310S SS	316L SS	321 SS
MgCl ₂ -KCl-NaCl		No specimen exposures due to extensive attack on 316L SS flanges and gas inlets and outlets during preparation of eutectic mixture				
	48	27		10	13	13
	168	28		11	14	14
NaCl-MgCl ₂	1000	29		12	15	15
	1000	33		03	03	04
		Anodized		Anodized	Welded	Welded
	48	11		13	16	16
	168	12		14	17	17
CaCl ₂ -NaCl	1000	30		15	18	18
	1000	32		04	05	05
		Anodized		Welded	Welded	Welded
	48	24	11		10	10
	168	25	12		11	11
Li ₂ CO ₃ -Na ₂ CO ₃ -K ₂ CO ₃	1000	26	24		12	12
	1000	34	22		04	03
		Anodized	Welded		Welded	Welded

*Targeted time

Post-tests, the aluminum alloy specimens were cleaned using a one minute dip in reagent grade nitric acid and the steel specimens were cleaned using a solution that was 10% nitric acid and 1% hydrofluoric acid in water while being ultrasonically agitated. All the specimens were rinsed in running water followed by ethanol and dried under forced-air and weighed. Pre- and post-tests, specimens were metallographically prepared and examined via optical and scanning electron microscopy. In some cases, microchemical analyses via energy dispersive analysis were performed.

3.0 RESULTS AND DISCUSSION

3.1 PRE-EXPOSURE

3.1.1 Anodized Al5052

The appearance of an anodized specimen Al5052 and its cross section are presented in Figure 7. The anodizing process coated the entire specimen following the contours of the surface including that of the surface of the drilled hole. Minor cracking and protrusion observed is believed to be due to metallographic preparation (Figure 8). The thickness of the anodized layer was measured three times at three different positions in the longitudinal direction and at two different position in the transverse direction. The average of these fifteen coating thickness measurements is 33.8 micron (0.0013 inch). This average measured thickness is approximately 68% of the targeted 50 micron (0.002 inch) of the matte finish (Microlox-Natural) targeted thickness. The microstructure of this Al-2.5 to 2.8 Mg- 0.15 to 0.35 Cr- 0.4 Fe (max)-0.25 Si (max) alloyed showed fine precipitates (Figure 8) which were determined via energy dispersive analysis on an SEM to contain Al and Fe, Al and Mg, or Al, Mg, and Si. These specimens were tested to determine if the anodizing providing any protection against corrosion in the various salts.

Figure 7. Anodized layer covered the entire specimen including on the surface of the hole drilled in the specimen prior to anodizing. The average coating thickness is 33.8 micron (0.0013 inch).

Figure 8. Cross section of Al5052 showing minor cracking in the anodized layer (top-left), a protrusion (top-right) and fine precipitates (top-right and bottom-center). The cracking and protrusion may be an artifact of metallographic preparation.

3.1.2 Stainless Steels

The microstructural appearance of type 304 SS, type 310S SS, type 316L SS, and type 321 SS are presented Figure 9. There are significant differences in grain size and morphology, and in the amount of inclusions among these steels. Type 304 SS and type 310S SS display, to some extent, equiaxed grains with type 304 SS showing the larger grain size and higher level of inclusions. Type 316L SS and, to a greater extent, type 321 SS display more blocky-type grains. Type 316L SS shows a smaller grain size and a higher level of inclusions as compared to type 321 SS. The as-received and Electron Beam autogenous welded to a depth of approximately one-half thickness stainless steel specimens are shown in Figure 10. These specimens were tested to determine whether the weld region performed differently in the various salts.

12-1074-04

304 S.S.

500X 10μm
10% Oxalic

12-1075-04

310 S.S.

500X 10μm
10% Oxalic

12-1076-04

316 S.S.

500X 10μm
Aqua Regia

12-1077-04

321 S.S.

500X 10μm
Aqua Regia

Figure 9. The appearance of the etched microstructures (500X magnification) of as-received type 304 SS (oxalic acid), type 310S SS (oxalic acid), type 316L SS (aqua regia) and type 321 SS (aqua regia). Note the differences in grain size and morphology, and inclusions.

Figure 10. Appearance of the stainless steel specimens after being Electron Beam autogenous welded to a depth of approximately one-half specimen thickness.

3.2 POST-EXPOSURE

3.2.1 Introduction

There were many significant events that occurred during the materials evaluation process. While difficulties with the chloride salts were anticipated, the degree of corrosiveness of the ternary chloride salt, MgCl_2 - KCl - NaCl, surpassed projections. Type 316 SS was chosen as the material of construction of the top flange of the ceramic reaction vessel and for the various gas inlets and outlets. After production of the eutectic salt mixtures, it was clear that all chosen materials for evaluation would fail in this ternary chloride salt. This severe corrosivity is very apparent in Figure

11, which presents an image of the external surface type 316L SS flange of one of the vessels that contained MgCl_2 - KCl - NaCl during its drying and melting. This flange, which shows brown product on its surface and significant yellowish-brown corrosion product on the outside of a sealing nut, is to be contrasted with that for one of the vessels that contained Li_2CO_3 - Na_2CO_3 - K_2CO_3 during the drying and melting process and for an additional 48 h of testing. The latter is nearly pristine. Purification of this salts will decrease the corrosivity and may allow economic use of steels. Hence this ternary salt should be further considered if use of cleaned salt is economically feasible.

Figure 11. Comparison of flanges of type 316L SS showing significant corrosion of the flange associated with the ternary chloride salt.

Another significant event was the failure of the zirconium wire used for holding the specimens to the mullite push-rod. This failure occurred in the chloride salt mixtures to varying extent. As shown in Figure 12, the wire remained attached to the push-rod. Based on post-exposure recovery of specimens, it appears that the build-up of the corrosion product between the wire and specimens led to the failure. In the cases, in which wire did not break, one specimen was removed from testing and the remaining specimens were secured with a large gauge wire. These initial wire failures led to varying exposure times for this evaluation.

**Specimens holder for Al 5052 after
48 h in $\text{CaCl}_2/\text{NaCl}$**

Figure 12. Failure of wire hold specimens to push-rods failed to varying extent in the chloride salts.

The next and most catastrophic event occurred just after the start of the final time interval of testing. Despite significant air flow in the exhaust system and many air changes per day within the room, the furnace control system suddenly degraded rapidly. The system crashed in the wee hours of the morning and all specimens were trapped within solid masses of salt. Evaluation of recorded information indicated that the failure started on the control segment for the CaCl_2 - NaCl reaction vessels and propagated. This event terminated further testing. All reaction vessels had to be broken apart and the solid mass of salt hammered into chunks small enough to retrieve the specimens. A few of the specimens were not recovered.

3.2.2 All Salts After Last Shut Down

The appearances of post-exposure, pre-chemical cleaned specimens of tested materials, for various times, are presented in Figure 13. Clearly obvious is that Al5052, regardless of being anodized or not, is rapidly destroyed in the chloride salts of interest. Al5052 and anodized Al5052 displayed reasonable resistance to the ternary carbonate, Li_2CO_3 - Na_2CO_3 - K_2CO_3 , salt. A direct visual comparison of the steels in this picture does not allow for performance comparison as the materials have not been descaled and were exposed for different times.

Figure 13. Appearance of specimens after final shut down. The specimens were exposed for differing time and inferences as to steels performance should not made. Clearly, Al5052, anodized or not, is not compatible with the chloride salts of interest.

3.3 REACTION RATES

3.3.1 $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ Eutectic Mixture

The reaction rates in $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic mixture are presented in Figure 14. As shown, the cumulative exposure reaction rates for all materials of containment decrease with increasing cumulative exposure time. These decreases indicate reactions that either are being driven by impurities, which are being consumed, or the development of a protective surface layer, which may be suggested by the appearance of the specimens in Figure 13. As shown in Figure 14, the steel performed progressively better than Al5052 as time is increased. Given that aluminum alloys tend to form more protective scales as compared to steels, consumption of impurities is the more likely explanation for the decreasing corrosion rates. This conclusion is further supported by the corrosion rate being the same for the anodized and not-anodized Al5052 specimens for the longest time shown in Figure 14. At the longest times, the steel specimens display similar corrosion rates for the welded and un-welded specimens, which indicates that welding of these steels do not affect their corrosion performance.

Figure 14. Cumulative corrosion rates of Al 5052 and steels in $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$. Note that the steels perform progressively better at longer times.

3.3.2 Binary Chloride Eutectic Mixtures

The corrosion rates for the binary chloride mixtures are presented in Table 1. As shown, these rates are very large. Al5052 in the anodized and un-anodized states were completely consumed. The very much lower corrosion rates of 310S SS in the NaCl-MgCl_2 eutectic mixture and 321 SS in the NaCl-CaCl_2 eutectic mixture as compared to the other materials in these mixtures may be due to slight differences in the temperatures of the reaction vessels or slight differences in the impurity content of the mixtures.

Table 1. Average corrosion rates in binary chloride eutectic mixtures

Material	Average Rate in NaCl-MgCl₂ [cm/y (mils/y)]	Average Rate in NaCl-CaCl₂ [cm/y (mils/y)]
Al5052	consumed	consumed
310S SS	-0.0246 (-9.7)	-0.5034 (-198.2)
316L SS	-0.1842 (-72.5)	-0.5543 (-218.2)
321 SS	-0.3916 (-154.2)	-0.0118 (-4.6)

3.4 METALLOGRAPHIC EVALUATIONS

4.0 CONCLUSIONS

5.0 REFERENCES

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