Phase 2 Final Report

Project Title: **Using Encapsulated Phase Change Material in Thermal Storage for Baseload Concentrating Solar Power Plants**

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Section 1 Executive Summary

Terrafore has successfully demonstrated and optimized the manufacturing of capsules containing phase-changing inorganic salts. The phase change was used to store thermal energy collected from a concentrating solar-power plant as latent heat. This latent heat, in addition to sensible heat increased the energy density (energy stored per unit weight of salt) by over 50%, thus requiring 40% less salt and over 60% less capsule container. Therefore, the cost to store high-temperature thermal energy collected in a concentrating solar power plant will be reduced by almost 40% or more, as compared to conventional two-tank, sensible-only storage systems. The cost for thermal energy storage (TES) system is expected to achieve the Sun Shot goal of $15 per kWh(t).

Costs associated with poor heat-transfer in phase change materials (PCM) were also eliminated. Although thermal energy storage that relies on the latent heat of fusion of PCM improves energy density by as much as 50%, upon energy discharge the salt freezes and builds on the heat transfer surfaces. Since these salts have low thermal conductivity, large heat-transfer areas, or larger conventional heat-exchangers are needed, which increases costs. By encapsulating PCM in small capsules we have increased the heat transfer area per unit volume of salt and brought the heat transfer fluid in direct contact with the capsules. These two improvements have increased the heat transfer coefficient and boosted heat transfer.

The program was successful in overcoming the phenomenon of melt expansion in the capsules, which requires the creation of open volume in the capsules or shell to allow for expansion of the molten salt on melting and is heated above its melting point to 550°C. Under contract with the Department of Energy, Terrafore Inc. and Southwest Research Institute, developed innovative method(s) to economically create the open volume or void in the capsule. One method consists of using a sacrificial polymer coating as the middle layer between the salt prill and the shell material. The selected polymer decomposes at temperatures below the melting point of the salt and forms gases which escape through the pores in the capsule shell thus leaving a void in the capsule. We have demonstrated the process with a commonly used inorganic nitrate salt in a low-cost shell material that can withstand over 10,000 high-temperature thermal cycles, or a thirty-year or greater life in a solar plant. The shell used to encapsulate the salt was demonstrated to be compatible with molten salt heat transfer fluid typically used in CSP plants to temperatures up to 600 °C.

The above findings have led to the concept of a cascaded arrangement. Salts with different melting points can be encapsulated using the same recipe and contained in a packed bed by cascading the salt melting at higher melting point at the top over the salt melting at lower melting point towards the bottom of the tank. This cascaded energy storage is required to effectively transfer the sensible heat collected in heat transfer fluids between the operating temperatures and utilize the latent heat of fusion in the salts inside the capsule. Mathematical models indicate that over 90% of the salts will undergo phase change by using three salts in equal proportion. The salts are selected such that the salt at the top of the tank melts at about 15°C below the high operating-temperature, and the salt at the bottom of the tank melts 15°C above the low operating-temperature. The salt in the middle of tank melts in-between the operating temperature of the heat transfer fluid. A cascaded arrangement leads to the capture of 90% of the latent-heat of fusion of salts and their sensible heats. Thus the energy density is increased by over 50% from a sensible-only, two-tank thermal energy storage. Furthermore, the Terrafore cascaded storage method requires only one tank as opposed to the two-tanks used in sensible heat storage. Since heat is transferred from the heat transfer fluid by direct contact with capsules, external heat-exchangers are not required for charging storage. Thus, the cost of the thermal storage system is reduced due to smaller containers and less salt. The optimum salt proportions, their melting temperature and the number of salts in the cascade are determined by raw materials costs and the mathematical model.

We estimate the processing cost of the encapsulation to be low, where the major cost of the capsule will be the cost of the phase-change salt(s). Our economic analyses show that the cost of EPCM-TES is about $17.98 per kWh(t), which is about 40% lower than the $28.36 per kWh(t) for a two-tank sensible heat TES for a large scale CSP-TES design. Finally, additional improvements in the heat-transfer fluids, currently in development elsewhere will further improve the energy density to achieve the SunShot goal of $15 per kWh(t).

The project was conducted in two phases:

Phase-1 was completed in January 2012, when Terrafore successfully developed a recipe for 5 mm capsules of potassium nitrate (KNO_3) salt with a melting point of 335°C. The shell material withstood temperatures up to 450 °C and 10 cycles in a differential scanning calorimeter. Scanning electron micrographs of cut-open capsules indicated a void in the middle. A mathematical model developed showed that the optimum capsule size is less than 15mm.

In Phase-2 the recipe was further optimized and the 5mm capsules were made using the now patented “Sacrificial-Layer” process withstood 5000 thermal cycles in a “HiTec” (mixture of nitrate salts) molten-salt mixture between 250°C and 450°C. High melting-point salts and salt-mixture prill can now be encapsulated in suitable shell-materials. The recipe to make capsules is sensitive to changes in shell and polymer material quality and composition. Seventeen experiments were designed (statistical D-optimal design used) by varying compositions of the selected chemical components of the recipe. Capsules made using these recipes were thermally cycled in the “TerraDipper”. One recipe successfully survived 5,000 thermal cycles. Two other recipes survived 2,500 thermal cycles**.** In each thermal cycle the salt in the capsule undergoes complete phase change.

A test rig, called the “TerraDipper”, was custom designed and tested successfully to automatically conduct thermal-cycle tests (≥ 10,000 cycles) using a nitrate-based molten salt, heat-transfer fluid. During testing, temperatures of 600°C were not used because heating the “HiTec” heat-transfer fluid to these temperatures requires a sophisticated handling and safety system, outside the scope of the program. However, selected capsules were successfully thermal cycled in a Thermal Gravimetric Analyzer (TGA) to 550°C for up to 10 cycles, indicating the shell can withstand these temperatures.

Even though the capsules remain intact, tests indicated that the “HiTec” salt entrained through the pores of capsules. The goal was to show that these capsules can withstand over 10,000 thermal cycles or the thermal cycles in the 30-year life of a plant with less the 0.1% breakage rate, between operating temperatures of a CSP system (300°C and 600°C). Program constraints did not permit the further refinement of the recipe, so as to ensure capsule longevity to 10,000 thermal cycles, by eliminating the capsule pores entrainment. Nevertheless, by depositing over 5 µm nickel coating on the capsule, the pores were effectively sealed. Future tests must test the efficacy of the sealing method employed.

A “tableting” method is used to make 10mm to 15mm capsules, which were termed as “beadlets”. Using this method, large batches of capsules can be produced quickly. It also significantly reduces the heat-treatment time, as the tablets possess adequate porosity or void volume. Porous “beadlets” cores were successfully prepared through the compression and “tableting” of KNO_3 powder. A pan-coating method was used to overcoat the tablets with same shells used in the sacrificial layer method. The over-coating of the “beadlets” was not consistent since these were not spherical and did not survive heat treatment. Further work is required to optimize the tablet preparation and coating conditions to yield a final product suitable for heat treatment and thermal cycling.

In conclusion, the program achievements and findings are vital to thermal energy storage in a concentrating solar power plant (CSP). It smoothes the cost-to-demand ratios for electricity and affords predictable power generation, especially on days of zero to intermittent sunshine and reduces the cost by almost 40% when compared to the conventional two-tank sensible storage system.

Section 2 Background

Thermal energy storage (TES) is essential to any concentrating solar power plant (CSP) as it is required for generating power smoothly and predictably, especially on days when there is no or intermittent sunshine and when the cost and demand for electricity is high. Currently, CSP plants use sensible energy storage in molten salt to store thermal energy which requires large volume of salt, two large tanks and cost about $30 per kWh(t) (1). To economically produce electricity from CSP, SunShot set the goal at $15 per kWh(t) for TES for a high-temperature CSP. Storing thermal energy in phase change material (PCM) such as inorganic salt mixtures, as latent heat of fusion in addition to sensible heat can increase the energy density for storage by as much as 50% requiring less salt and hence can reduce the cost to potentially achieve the SunShot goal (2).

Although thermal energy storage that relies on the latent heat of fusion of PCM improves energy density, upon energy discharge the salt freezes and builds on heat transfer surfaces. Since these salts have low thermal conductivity, large heat transfer surfaces areas or larger conventional heat exchangers are needed to maintain design heat rate requested by power plant, which increases costs. Therefore to obtain specified heat transfer rates, either the heat transfer coefficient must be increased by actively removing the salt from the surface and / or by increasing the thermal conductivity or large heat transfer surfaces must be provided by using cost-effective method or both heat transfer coefficient and heat transfer area must be increased.

Several methods are described in literature to increase the heat transfer coefficient by physically removing the salt as it freezes on the heat exchanger surfaces. These methods were either unsuccessful and / or not practical for use in large scale power plant. For example, LeFrois, Mathur (3) used scrapers to continuously remove the solid freezing on the heat exchanger tubes to improve heat transfer coefficient. Mathur (4) pumped freezing slurry of a hyper-eutectic molten salt mixture onto coated heat exchanger tubes to freeze and remove the solid using fluid forces. Recently, with contracts from Department of Energy (2), University of Connecticut used an intermediate fluid to transfer energy from freezing PCM to heat exchanger tubes using gravity assisted wickless heat pipes and showed a two-fold increase in heat transfer coefficient. Many of these active methods, though commonly used in process industries are not practical for large scale power plants because they require either complex heat exchangers or sophisticated maintenance and operating procedures or both.

Encapsulating PCM material inside small capsules increases the specific surface area and by using heat transfer fluid in direct contact with these capsules increases the heat transfer coefficient. Thus, both heat transfer coefficient and heat transfer area is increased. However, a technical barrier with encapsulating salts is that an open volume or void must be created inside the capsule when it is produced. This void is necessary to accommodate the volume increase when salt melts and expands on heating. Lehigh University (5) fabricated 5 cm cylindrical capsules made of Nickel and partially filled it with Zinc and/or eutectic mixtures of $MgCl_2$-NaCl. Similarly, University of Florida (6) successfully made 2 cm to 5 cm capsules of sodium nitrate which survived over 200 thermal cycles. These studies are ongoing and results are not available. However, economic analysis using a mathematical model of encapsulated PCM using a nitrate salt mixture showed that the capsule diameter should be less than 15mm (a 12mm is recommended). The smaller capsules having a specific heat transfer surface to volume of PCM capsule results in maintaining design heat rates till 90% of the PCM goes through phase change.

A key success factor for using capsules for thermal storage is that the cost of encapsulation must be low. Terrafore' s approach uses commercially available fluid bed coaters and tableting machines commonly used to make capsules for agricultural, food and pharmaceutical industries and hence does not require significant capital investment. However, even though encapsulation is common, much of the work on encapsulating PCM has been done for low temperature PCMs (7) (8) (9).. While work on encapsulating a high temperature PCM such as sodium nitrate, has seldom been attempted. This project used work done by others to address the issues that occur when PCMs are encapsulated at high temperatures. As stated earlier, one of the issues with encapsulating a PCM at high temperature is the difference in thermal expansion of the core material and the shell material and the difference in volume of the core material when it changes phase. This volume change can build stresses inside the shell which can rupture the shell and cause the PCM to leak out. Another issue is the thermal stability and toughness of the shell material to withstand thousands of freeze-thaw-cycles, a basic requirement for using this as thermal storage material. In addition, the encapsulated material must be thermally conductive. Our approach modified one of the well-known processes used for encapsulation to create a void inside the capsule during formulation by decomposing a sacrificial component (such as an organic polymer) mixed with the core material or coated along with the shell material. The method of using a sacrificial component, which is described later in the document, is an innovative extension of this research.

Section 3 Introduction

STATEMENT OF PROJECT OBJECTIVES

The objective of the project is to economically produce 5 mm to 15 mm size capsules that contain inorganic salt / and or salt-mixtures. These capsules are used to store thermal energy as a combination of latent heat of fusion and sensible heat. The shell used to encapsulate the salt must be compatible with a molten salt heat transfer fluid heated to temperatures up to 600°C and must be robust to withstand over 10,000 thermal cycles between 300°C and 600°C. The breakage rate, if any, must be less than 0.1% per year. These operating requirements are typical of a CSP plant. The breakage rate is specified as an ambitious goal to minimize the life cycle cost of plant. To achieve the SunShot goal of $15 per kWh(t) for thermal storage system, the capsule cost must be less than $5 per kWh(t).

GO / NO-GO MILESTONES

The success metrics for the capsules must meet the targets shown in Tables 1 and 2.

Table 1. The success metric for isothermal hold Failure Rate of the encapsulated phase change material.

Constant Temperature	Variable 1 (Time)	Evaluate: ∂(**h**)/∂(**t**)†
Success Metric	1 Year	≤0.1%
Current Process	1 Year	Unknown

†Evaluation of the rate of change in the hazard function with respect to time must produce either a constant that is below the acceptable threshold or a function that converges to a value that is below the threshold. Units of time should be considered in years.

Table 2. The success metric for thermal cycling Failure Rate of the encapsulated phase change material.

Temperature Cycling	Variable 2 (Temperature)	Evaluate: ∂(**h**)/∂(**t**)†
Success Metric	290-600 °C	≤0.1%
Current Process	290-600 °C	Unknown

†Evaluation of the rate of change in the hazard function with respect to time must produce either a constant that is below the acceptable threshold or a function that converges to a value that is below the threshold.

The viability of encapsulated phase change technology is dependent on the thermal decomposition of the sacrificial polymer coating. This is a critical component of the system as it is required to generate the void space needed for the PCM to expand into upon melting and absorption of additional sensible heat. The thermal decomposition of this polymer layer currently requires careful treatment over a period of two days around the decomposition temperature of 250 °C to 280 °C.[3] While this is a one-time treatment, it is very sensitive and can result in failure of the encapsulation shell. Table-3 specifies the success metric specific to the concept for making capsules.

Table 3. The success metric for thermal decomposition encapsulated phase change of the sacrificial polymer layer contained within the material.

	Time (h)	Temperature (°C)
Success Metric	<48	≤250
Current Process[†]	48	250

THERMAL STORAGE REQUIREMENTS

Storing heat collected from concentrating collectors and delivering heat from thermal storage to power plant has specific requirements for discharging at or near design temperature and at heat rates demanded by power plant, and for charging at heat rates designed to collect solar energy from solar concentrators. The thermal storage system must deliver the requested heat rate irrespective of the amount of energy remaining in the storage tank. Thermal storage is considered completely discharged once the delivered temperature and / or heat rate is lower than a cut-off point . Thermal storage is considered completely charged when the temperature of heat transfer fluid out of storage is higher than a cut-off temperature. This design requirement generally applies to phase change storage systems since the heat rate towards end of discharge cycle decreases as PCM material builds on heat transfer surface.

Another key requirement for PCM thermal storage using capsules is that the capsules must withstand over 10,000 thermal cycles (equivalent to a 30-year diurnal cycles) between CSP operating temperatures of 250°C to 600°C with low breakage rate. An acceptable breakage rate of 0.1% per year is specified as a milestone for this project. Also, the broken material, if any, should not interfere with the heat transfer and transport properties of the heat transfer fluid the capsules are in direct contact with.

INNOVATIVE METHOD TO MAKE CAPSULES

A key success factor for encapsulating salts in suitable shell materials is to economically create a void inside the shell to accommodate for volume change on melting and heating. This volume change of salt can be as much as 10% to 25% depending on the selected PCM-salt or PCM-salt mixture.

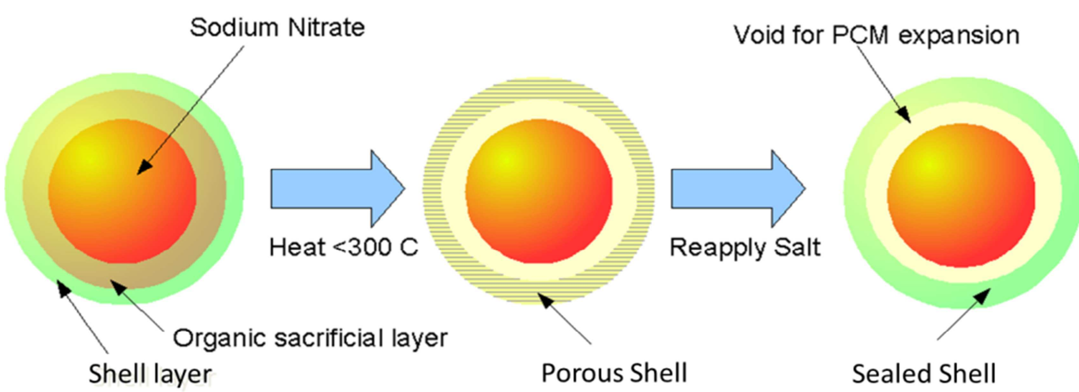

Figure 1. A polymer layer between shell and prill is decomposed to gas to create a void in the capsule.

Figure 1 shows a schematic of the patented concept for creating a void in the capsule. The process consists of first applying a layer of sacrificial polymer on a salt prill of selected diameter and another coating containing a mixture of binder and inorganic shell material. A fluid-bed coater is used to coat these layers onto the prill. The capsule thus produced is then slowly heated in a furnace to decompose the polymer and organic binder to gas that escapes through the shell leaving a void around the salt in the capsule. The fluid bed encapsulation process is commonly used in the industry and no special equipment is required to produce the capsules.

Coating formulations are composed of a binder, film former, inorganic filler, and surfactant. Salts melting at different melting points can be encapsulated using this method. There are several factors discussed later, which are considered in formulating the recipe to produce robust capsules.

Significance of Terrafore' s innovative approach to capsules uses common industrial coating method such as fluid-bed coaters and also the selected shell material cost is low. Even though encapsulation is a common method used for pharmaceutical and agricultural products, encapsulating high temperature materials such as described here has never been done before.

CASCADED PACKED BED THERMAL ENERGY STORAGE

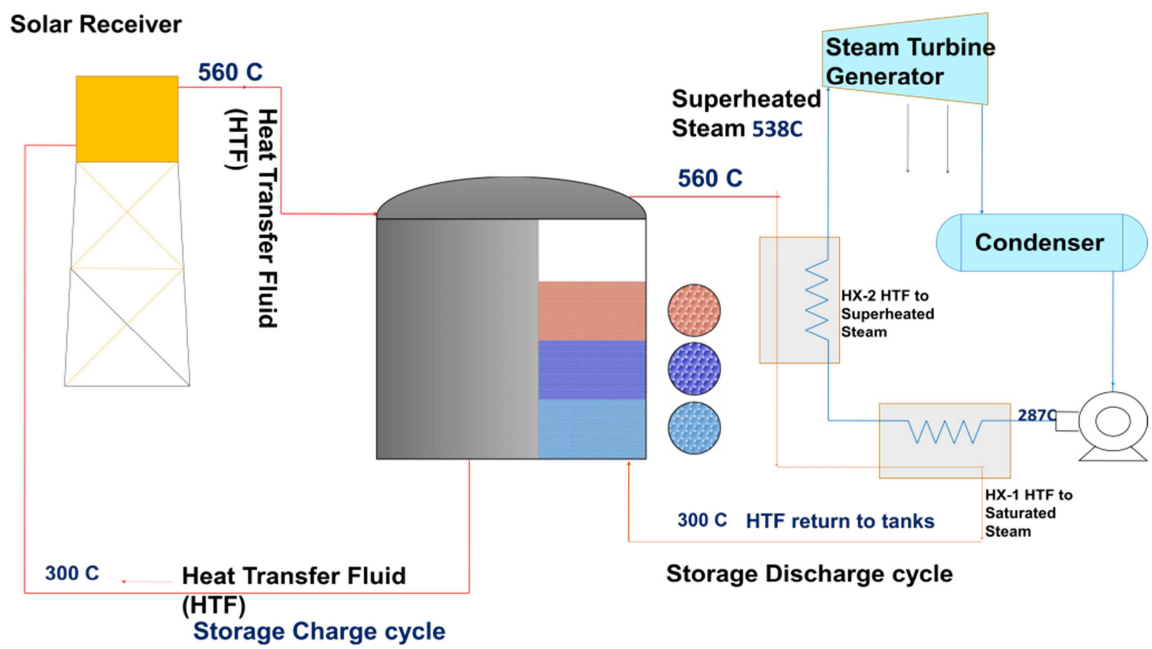

Figure 2. Cascaded encapsulated phase change storage tank with tower solar receiver and Rankine steam turbine power generator shows heat transfer fluid flow during storage charge and discharge cycles.

Capsules are contained in a packed bed with heat transfer fluid filling the open space between the capsules. Energy is stored as latent heat of fusion and sensible heat of salt inside the capsule and as sensible heat of heat transfer fluid in the space not filled by capsules in the tank. Figure 2 shows a thermal energy storage tank using three different PCMs in capsules and stacked in the tank. PCM with highest melting point (about 545 °C) is at the top of the tank and capsules with PCM melting at the lowest melting point, such as 315 °C, is at the bottom of the tank. The selection of melting points is an optimization problem and determined using mathematical models (10) presented in Phase 1. During the storage charge cycle, the hot HTF from the solar collector-receiver is pumped through the top of the tank. As the fluid flows down through the packed bed of capsules in the storage tank it transfers the collected heat to melt the salt in the capsules and heat it. As HTF cools it meets progressively lower melting salt capsules and exits the tank at the bottom of the tank and is returned to the solar collector.

During the storage discharge cycle, the HTF from the top of the storage tank is pumped through the power block heat exchangers through the superheater HX-2 and then to high pressure boiler-preheater HX-2 to boil water from condenser and superheat steam. The superheated steam is introduced into the steam turbine generator to generate electricity. The cold HTF typically at 300 °C exiting from the boiler-preheater HX-1 is returned to the bottom of the storage tank. HTF as it flows up through the tank is heated by transferring heat from the salt which freezes inside the capsules. The tank is thermally stratified with hot HTF fluid at the top and cold fluid at the bottom of the tank. The delivered temperature to the power block heat exchangers remains constant at 560 °C till the thermocline reaches the top and the storage discharge cycle is stopped when the delivered temperature drops below a cut-off temperature which is typically 545 °C (15C lower than the top operating temperature).

Because of latent heat, the specific heat capacitance of the capsules is high and therefore a good thermal stratification is maintained. Cascading is achieved by using progressively higher melting point salts in the capsules which are placed in the tank from bottom to top. The lowest melting salt capsules are at the bottom and highest melting point capsules are at the top. In Figure 2 three different types of salt capsules are shown. The salts are selected such that melting point of the salt at the top of the tank is a few degrees lower than the high operating temperature of HTF and the melting point of salt at the bottom of the tank is a few degrees higher than the lower operating temperature of the HTF. Results with the mathematical model described later, indicate these melting points should be the cut-off point temperatures. The cut-off point temperatures are the temperatures at end of charge and discharge cycles. For example, the discharge cycle the HTF temperature delivered to steam generator HX-2 remains constant at the high operating temperature and begin to decrease when about 95% of energy stored is depleted. The temperature begins to decrease till the cut-off temperature when it is deemed as fully discharged. Similarly, during charge cycle, the storage is deemed completely charged when the exit temperature from the tank begins to increase to the cut-off temperature. This cut-off temperature is typically 15C from the design operating temperatures of 560 °C and 300 °C shown in Figure 2. The higher melting point of the salt should be about to 545 °C and lowest melting point of salt at bottom of tank should be about 315 °C. Other factors such as availability and cost should be considered in selecting the salts.

KEY FINDINGS

In Phase-1, we were successful in overcoming the phenomenon of melt expansion in the capsules, which requires the creation of open volume in the capsules or shell to allow for expansion of the molten salt on melting and heating to above its melting point to 550°C. We successfully met the milestones and developed a recipe to encapsulate a nitrate salt melting at 335°C in 5mm capsules in a suitable shell material that withstood temperatures to 450°C and upto 10 cycles between 250°C and 450°C in a laboratory differential scanning calorimeter. Scanning electron micrographs of cut-open capsules indicated a void in the middle.

Phase 2 resulted in optimizing recipe using the now patented "Sacrificial-Layer" method which produced capsules that withstood up to 5000 thermal cycles between 250°C and 450°C in a test rig called the "TerraDipper". The test rig was custom designed and tested successfully to automatically conduct thermal-cycle tests (≥ 10,000 cycles) using a nitrate-based molten salt, heat-transfer fluid, Hi-Tec". During testing, temperatures of 600°C were not used because heating the "HiTec" heat-transfer fluid to these temperatures requires a sophisticated handling and safety system, outside the scope of the program. However, selected capsules were successfully thermal cycled in a Thermal Gravimetric Analyzer (TGA) to 550°C for up to 10 cycles, indicating the shell can withstand these temperatures. Even though the capsules remain intact tests indicated that the "HiTec" salt entrained through the pores of capsules between 2500 and 5000 thermal cycles. Program constraints did not permit the further refinement of the recipe, so as to ensure capsule longevity to 10,000 thermal cycles, by eliminating the capsule pores entrainment. Nevertheless, by depositing a 5 µm nickel coating on the capsule, the pores were effectively sealed. Future tests must test the efficacy of the sealing method employed.

A mathematical model (10) (11) developed showed that the optimum capsule size is less than 15mm. The mathematical model led to the concept of a cascaded arrangement. Salts with different melting points can be encapsulated using the same recipe and contained in a packed bed by cascading the salt melting at higher melting point at the top over the salt melting at lower melting point towards the bottom of the tank. This cascaded energy storage (described later) (12) is required to effectively transfer the sensible heat collected in heat transfer fluids between the operating temperatures and utilize the latent heat of fusion in the salts inside the capsule. Mathematical model indicate that over 92% of the salts will undergo phase change by using three salts in equal proportion inside capsules of 12mm in diameter. The salts are selected such that the salt at the top of the tank melts at about 15°C below the high operating-temperature, and the salt at the bottom of the tank melts 15°C above the low operating-temperature. The salt in the middle of tank melts in-between the operating temperature of the heat transfer fluid. A cascaded arrangement leads to the capture of 90% of the latent-heat of fusion of salts and their sensible heats. Thus the energy density is increased by over 50% from a sensible-only, two-tank thermal energy storage. Furthermore, the Terrafore cascaded storage method requires only one tank as opposed to the two-tanks used in sensible heat storage. Since heat is transferred from the heat transfer fluid by direct contact with capsules, external heat-exchangers are not required for charging storage. Thus, the cost of the thermal storage system is reduced due to smaller containers and less salt. The optimum salt proportions, their melting temperature and the number of salts in the cascade are determined by raw materials costs and the mathematical model.

We estimate the processing cost of the encapsulation to be low, where the major cost of the capsule will be the cost of the phase-change salt(s). Our economic analyses show that the cost of EPCM-TES is about $17 per kWh(t), which is almost 50% lower than the $30 per kWh(t) for a two-tank sensible heat TES for a large scale CSP-TES design. These costs will be less than $15 per kWh when heat transfer fluids with higher specific heat (under development elsewhere) become available.

To reduce processing time to make capsules, a “tableting” method is used to make 10mm to 15mm capsules, which were termed as “beadlets”. Using this method, large batches of capsules can be produced quickly. It also significantly reduces the heat-treatment time, as the tablets possess adequate porosity or void volume. Porous “beadlets” cores were successfully prepared through the compression and “tableting” of KNO_3 powder. A pan-coating method was used to overcoat the tablets with same shells used in the sacrificial layer method. The over-coating of the “beadlets” was not consistent since these were not spherical and did not survive heat treatment. Further work is required to optimize the tablet preparation and coating conditions to yield a final product suitable for heat treatment and thermal cycling.

Section 4 Results and Discussion

The following is a summary of major tasks reported in the following section

- Task 1: Prepare several samples of capsules
- Task 2 Conduct Tests for Durability and Longevity of Capsules
- Task 3: Make large capsules (approx. 10 mm) using Tableting and pan coating method.
- Task 4. Scale-up and economic analysis

TASK 1. MATERIAL SELECTION AND RECIPE FOR MAKING CAPSULES

A successful recipe was developed after experimenting with various combinations of materials and composition with the innovative sacrificial polymer methods, described later. The materials included:

- Sacrificial materials: Hydroxypropyl Cellulose (HPC), Hydroxypropyl Methyl Cellulose (HPMC)
- Binders: Ceramabind 380 and Ceramabind 6441A,
- Film formers: Zein, HPMC, Ethylcellulose (Ethocel), polyvinyl chloride (PVC), and mixtures thereof , clay, Surfactant: Sorbitan mono-oleate
- Solvents for coating solutions: water, acetone, tetrahydrofuran
- Inorganic fillers: silica, micronized stainless steel, Cloisite 30B, natural montmorillonite clay (Cloisite Na+)
- Shell materials considered: Clay, Kaolin mixed with Clay, stainless powder, and mixtures

Potassium nitrate (KNO_3) salt was chosen as the PCM because prills of this salt are readily available and it has a low thermal expansion on melting. Other salts can be used but will require prilling to the required particle size.

Fluid bed coating was identified as the preferred encapsulation process, and a variety of formulations were developed for coating nitrate salt prills. Thermal studies were used to measure the performance of the coatings and help in refining the formulations.

Fluid bed coating, also referred to as air suspension coating, is a common encapsulation technique used for applying coating to solid particles. A schematic and picture of the process are shown below in Figure 3. Solid particles are first fluidized on a bed of air to create a constant recycling of particles suspended in air. A fine mist of coating solution is then sprayed into the chamber to coat the solid particle as they are suspended. Longer coating times result in thicker coatings. Furthermore, coating solutions can be switched to introduce multiple coating compositions. This is the only process currently being used for the overcoating of nitrate salt beads. The coater being used is a Fluid Air Fluid Bed Feasibility Processor.

Formulations and Heat Treatment Recipe

Our innovative concept shown in Figure 4, to make the capsules consisted of applying two layers, where the first inner layer is sacrificial and the outer layer is composed of inorganic material. Once the outer layer is in place, the inner layer is removed via thermal decomposition to leave a void inside the capsule for accommodation of salt thermal expansion. For salts that are reactive, such as KNO_3, a triple layer coating system was developed to slow down or prevent any potential reaction between the salt and the organic sacrificial material. Both the double-layer and triple layer methods shown in Figure 5 have been patented.

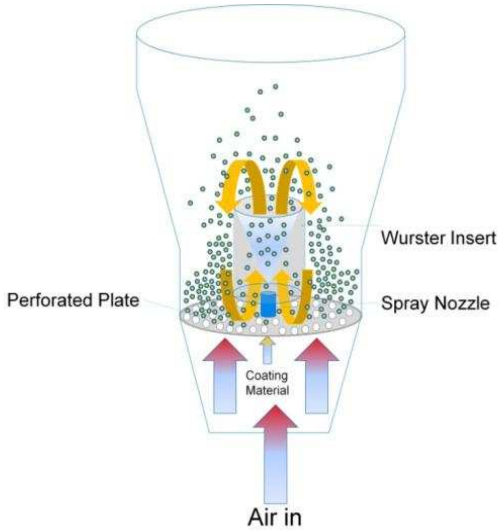

Figure 3. Fluid bed coating schematic (left) and picture (right).

Three major steps are involved in selecting the best formulation and recipe to produce robust capsules

1. Type and composition of binder, polymer
2. Type and thickness of shell coating
3. Recipe for heat treating to decompose polymer

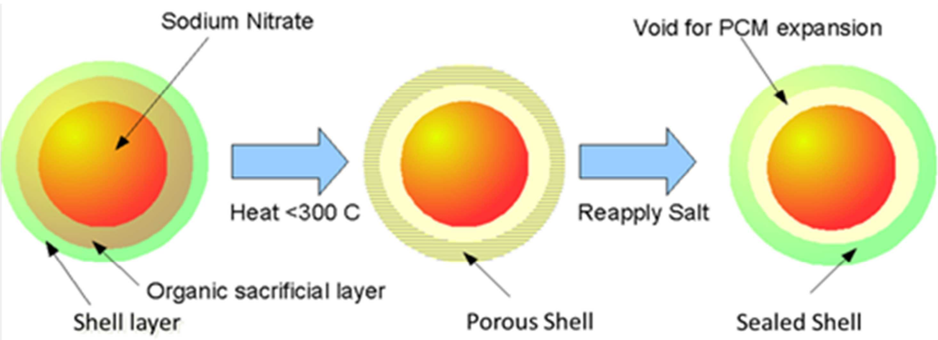

Figure 4. Encapsulation formulation concept.

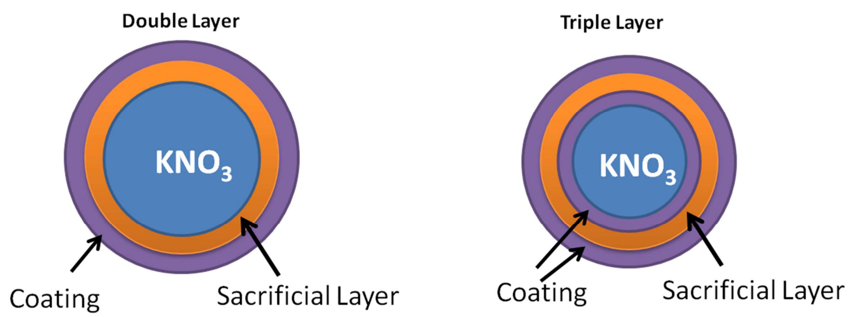

Figure 5. Schematic of Double Layer and Triple Capsules.

In Phase 1, more than 100 experiments were conducted with combinations of formulations, various thicknesses of shell, and different amounts of polymer as sacrificial material.

The recipe selected to make the capsule, referred to as MOM recipe (patented Mathur-Oxley-Mendez recipe) consists of: (specific percentages are proprietary)

- Inner Shell, 9.0% wt.(16% wt. of initial prill)
    - montmorillonite clay, Cloisite NA+
    - alumina from Ceramabind 644A (binder)
    - ethyl cellulose, Ethocel E4 (film former)
    - Deposited from water/ethanol blend
- Middle Sacrificial Layer, 12.4% wt. (19% wt. of initial prill)
    - Hydroxypropyl methyl cellulose (HPMC)
    - Deposited from water
- Outer Shell, 22.5% wt. (29% wt. of initial prill)
    - montmorillonite clay, Cloisite NA+
    - alumina from Ceramabind 644A (binder)
    - ethyl cellulose, Ethocel E4 (film former)
    - Deposited from water/ethanol blend

The capsules were heat treated in a furnace at 0.1C /min with an 8 hour hold at 280 °C (the decomposition temperature of the polymer) and continued heating at 0.1C/min to 450 °C. The capsules were then examined in optical microscope and SEM and were subjected to thermal cycling for 10 cycles in a DSC.

Formulation Repeat - Scientific Underpinnings of Clay Homogenization on Porosity and Strength of Shell

To validate the original successful formulation from Phase I and ensure a consistent foundation for further optimization experiments, the formulation developed in Phase I was successfully repeated. However, in one of the repeats, we noticed the capsules sample PII-13 failed, shown figure 6, when heat to 280C. Analysis of process steps indicated the mixing time for clay was longer and the clay was well homogenized. To confirm if the mixing time was a factor, we prepared a second sample, Sample PII-16,with minimal mixing using an overhead stirrer at less than 1000 rpm to disperse the clay. The results are shown in Figure 7 The capsules prepared with non-homogenized clay survive up to 330 °C and, upon cross sectioning, show an inner morphology consistent with the observations in Phase I. Furthermore, when heated to 500 °C for 24 hours the capsules survived. (See picture on right in Figure 7).

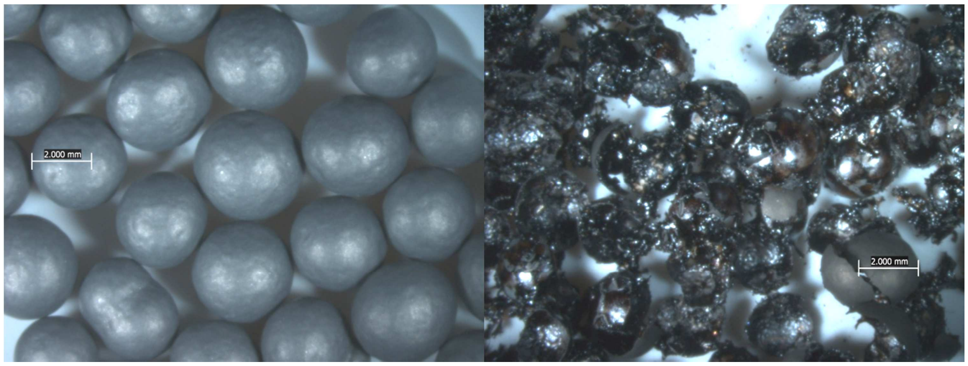

Figure 6. Optical micrographs of capsules, sample PII-13, with outer shell prepared from homogenized clay dispersion. Left: as prepared; Right: heated to 280 °C.

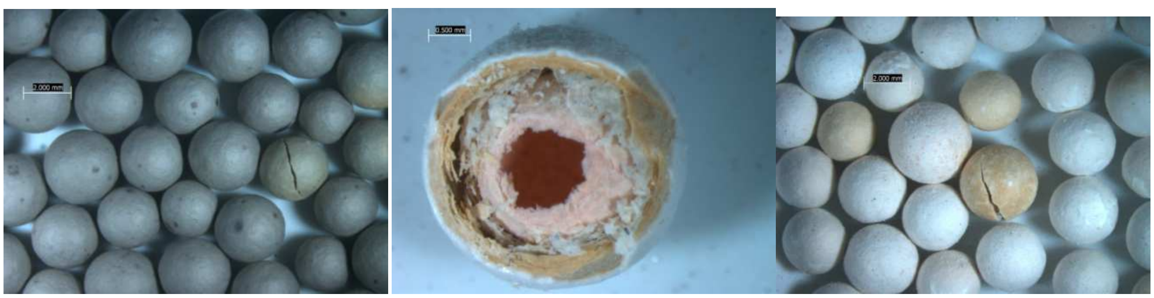

Figure 7. Optical micrographs of (left) capsule, Sample PII-16, heated to 330 °C, (middle) cross-section of capsules heated to 330°C, and (right) capsules heated to 500 °C.

Fortuitously, this observation was important because the Cloisite Na^+ clay material obtained from Southern Clay Products in Phase 1 was replaced by a new material RXG-7203 of same composition but better properties for strength. It was immediately noticed that the new clay dispersed more rapidly without the need for homogenization, indicating rapid exfoliation and increased solution viscosity. A test batch of capsules prepared with this material resulted in capsule failure at 280 °C.

As expected and based on the observed dispersion of the clay, both new clay materials failed to produce capsules that could withstand temperatures up to 315°C. To introduce additional gas permeability into the capsule shell, calcium carbonate was included as an additive at 20%. Calcium carbonate is a porous inert mineral commonly used as inexpensive filler for inorganic systems. Microparticles of calcium carbonate were dispersed with the clay prior to applying the outer coating layer. The function of the calcium carbonate was to first disrupt the brick-like formation of a gas barrier as the clay platelets dried on the surface of the capsule, and secondly introduce porosity into the shell through the calcium carbonates natural pores. Shell material with 80% new clay batch material and 20% calcium carbonate ($CaCO_3$) was successfully heated to 450°C. The combination of clay and $CaCO_3$ was further explored with 10% and 30% $CaCO_3$ blended with the new batch of Cloisite Na+ montmorillonite clay. As seen in Figure 8, when heated to 350°C the sample with 10% $CaCO_3$ remains intact while the sample with 30% is only partially intact.

The influence of clay homogenization time is a key observation to understanding the stability of the capsules and the source of capsule failure during heat treatment. The montmorillonite clay used for this work is a lamellar material consisting of platelets that are a few nanometers thick with depth and widths of over 100 nm. When dispersed in water, the natural clay begins to exfoliate into the individual platelets. When additional shear force is applied, such as homogenization, exfoliation is accelerated (13) (14). As an exfoliated solution dries in the presence of other ingredients, such as film formers and binders, the platelets can form a brick-like network with superior barrier and mechanical properties. Less exfoliation results in reduced barrier properties. It is hypothesized that the increased homogenization results in a tighter gas barrier for the microcapsule. The resulting tighter gas barrier slows the diffusion of gas into or out of the capsule. During decomposition of the sacrificial layer, the gas is unable to escape the capsule and ruptures due to internal pressure. Conversely, with no homogenization and minimal clay exfoliation, the capsule shell is more permeable to the decomposition gasses and allows for the successful heat treatment shown in Figure 8. The drawback of this approach is the reduced mechanical strength associated with less exfoliation.

While the use of $CaCO_3$ was successful for an outer shell composition, the viscosity of the mixture used for coating was high. Higher viscosity requires dilution for adequate fluid bed spraying, which results in significantly longer coating times. Combined with similar issues discussed below for coating beadlets, a more concentrated coating solution was developed. To increase gas diffusion through the clay composite barrier and decrease the coating solution viscosity, the clay was switched from montmorillonite to kaolin. Kaolin has a much lower aspect ratio, resulting in a reduction in gas barrier properties (15) (16). However, complete replacement of the montmorillonite with kaolin resulted in a shell material that was too brittle, which was evident through loss of coating fragments during routine handling of the capsules. To increase the strength, varying amounts of montmorillonite clay were added in for intercalation between the kaolin platelets. This mixture results in a coating solution that contained 15-20% solids versus the 2% solids concentration typically used with initially developed clay coating system. The viscosity of the Cloisite Na+ solution prevents the use of higher concentrations without the use of kaolin. Kaolin has a less significant impact on solution viscosity. The inclusion of Cloisite Na+ clay at 10-20% by weight added strength and enabled the formation of a less brittle shell. Figure 9 shows images of capsules with 80% kaolin and 20% Cloisite Na+ in the outer shell, along with the ethyl cellulose film former and alumina binder. With a few exceptions, the sample survives heat treatment to 450°C. This performance is comparable to the capsules prepared in Phase I.

Reformulation – Middle Layer

An additional change to the overall capsule formulation was a substitution of the middle layer, replacing hydroxypropyl methylcellulose (HPMC) with hydroxypropyl cellulose (HPC). HPC and HPMC have similar thermal decomposition profiles. The change was made to accelerate deposition of the second layer during microcapsule formulation. HPMC is only water soluble and was difficult to deposit onto the capsule. HPC is both water and solvent soluble, allowing for its quicker deposition from ethanol. No change was observed in the formation of the void when switching from HPMC to HPC, as seen in Figure 9.

Figure 8. Images of samples PII-25 and PII-26, with 10% and 30% $CaCO_3$in the shell, after heating to 350 °C.

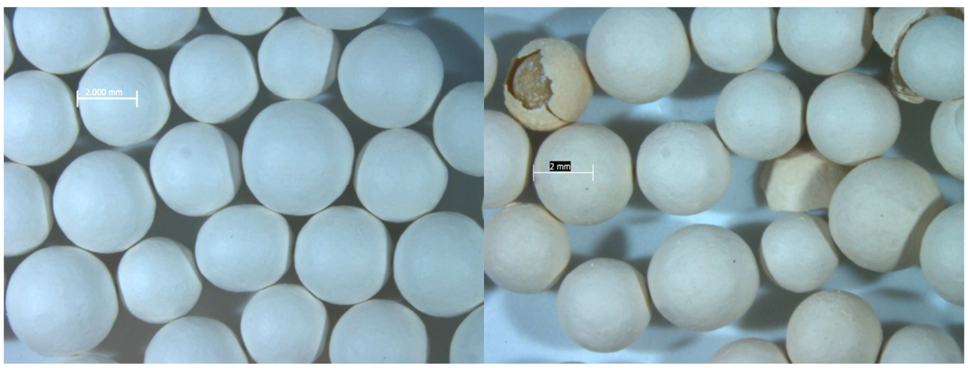

Figure 9. Images of PII-36 before and after heat treatment to 450°C. PII-36 is composed of a 20:80 montmorillonite:kaolin outer shell and HPC middle layer.

Design of Experiment for Optimizing Recipe Composition

Capsule optimization started with setting up a design of experiments (DoE) to test multiple variables related to the capsule construction. An increase in durability must be addressed through modifications of the capsule shell chemistry. There are three layers with multiple components in each layer. A list of the variables are shown below in

Table 4, along with current values, and represent the four capsule components of the core, inner layer, middle layer, and outer layer. This list served as the foundation for developing the DoE, based on the potential impact a variable adjustment may have on final capsule performance. For example, the inner layer separating the salt core from the sacrificial middle organic layer will not have a substantial impact on the capsule durability if minor formulation changes are made. Therefore, it was unchanged. The variables that should have the greatest impact on capsule durability are middle and outer layer thickness, and outer layer composition. Outer layer composition can be modified through the use of different inorganic material, binders, or film formers. In addition to layer thickness, the inorganic material will be the focus of increasing capsule durability. Layer thickness is adjusted by decreasing or increasing the coating time in the fluid bed coater.

Based on the multiple variables used to prepare the microcapsules a designed recipe was developed. After a review and ranking of the variables listed in

Table 4, the information was consolidated into 17 key experiments, not including duplicates, shown in

Discussion of Results after Heat Treatment of Capsules

Images of some of the formulations shown in Table-5 before and after heat treatment are shown in Figures10, 11,12,13,14,15,16,17,18,19,20,21,22,23. As indicated in Table-5, several of the samples either fused or fell apart on heat treatment in furnace. Only samples PII-34, PII-36, PII-39,and PII-57 remained intact and were selected for thermal cycling tests. The results for these are discussed in next section.

Table 5.

ICON

ICON represents the concentration by weight percent relative to the Kaolin clay base in the outer capsule layer. As described previously, the use of a new batch of clay beginning in Phase II of this project resulted in capsules that ruptured during heat treatment. Tests suggest that 10% and 20% montmorillonite added to the kaolin results in capsules that remain intact during heat treatment. Therefore, these values were chosen for inclusion in the experimental matrix in

Discussion of Results after Heat Treatment of Capsules

Images of some of the formulations shown in Table-5 before and after heat treatment are shown in Figures10, 11,12,13,14,15,16,17,18,19,20,21,22,23. As indicated in Table-5, several of the samples either fused or fell apart on heat treatment in furnace. Only samples PII-34, PII-36, PII-39,and PII-57 remained intact and were selected for thermal cycling tests. The results for these are discussed in next section.

Table 5.

BCON

BCON represents the concentration of Ceramabind binder included in the outer shell, compared to the amount used in the original Phase I formulation. The ceramic binder used, Cerama-Bind 644A, is a colloidal suspension of alumina used to provide mechanical stability for the shell after heat treatment. The original formulation from Phase I used a final shell composition that contained 18% Ceramabind material. In an effort to increase the strength of the capsules, a double concentration of Cerama-bind was considered as part of the experimental test matrix in

Discussion of Results after Heat Treatment of Capsules

Images of some of the formulations shown in Table-5 before and after heat treatment are shown in Figures10, 11,12,13,14,15,16,17,18,19,20,21,22,23. As indicated in Table-5, several of the samples either fused or fell apart on heat treatment in furnace. Only samples PII-34, PII-36, PII-39,and PII-57 remained intact and were selected for thermal cycling tests. The results for these are discussed in next section.

Table 5.

OUTER

. OUTER refers to the total weight percent concentration of the final outer layer relative to the total weight of the capsule. The weight percent of the outer layer was originally set at 29% for the successful Phase I formulation, which corresponds to 25.3% after heat treatment. To increase the KNO_3 payload, lower outer layer concentrations were considered at 24% and 19%. After heat treatment, the deposition of a 19% outer layer results in final outer coating weight of 16.7%.

MIDDLE

MIDDLE refers to the total weight percent concentration of the middle hydroxypropyl cellulose (HPC) relative to the total weight of the capsule. The middle layer is the critical layer for production of the void. The original formulation was based on the use of 19%, by weight, of hydroxypropyl cellulose (HPC) in the final capsule. After heat treatment and assuming 10% residue remaining, the final void left in the capsule is 31.8% by volume relative to the core material. This volume is excessive for the anticipated approximate 10% volume expansion of the salt. The overestimate was used to accommodate any higher residuals from HPC decomposition and to demonstrate the initial concept that a void would accommodate salt expansion. To further optimize the capsule formulation and increase the KNO_3 payload, the middle layer composition was tested at 10% and 6% by weight relative to the total weight of the capsule. The lower 6% target results in a void volume of 12.8% relative to the KNO_3 core size.

These formulations were all prepared using fluid bed coating, followed by heat treatment.

Table 4. Formulation Variables

	Description	Original Value
Salt Core	Material	Potassium nitrate
	Size	2-3 mm
	Distribution	N/A
First Layer	Inorganic material	Cloisite Na+
	Inorganic concentration	
	Ceramic binder	Ceramabind 644A
	Ceramic binder concentration	
	Film former	Ethocel
	Film former concentration	
	Material Ratios	
	Layer thickness	9 wt. %
Second Layer	Sacrificial material	HPMC

	Sacrificial concentration	
	Layer thickness	19 wt. %
Third Layer	Inorganic material	Cloisite Na+
	Inorganic concentration	
	Ceramic binder	Ceramabind 644A
	Ceramic binder concentration	
	Film former	Ethocel
	Film former concentration	
	Layer thickness	29% wt.
	Clay dispersion technique	Overhead stirrer, overnight
Heat treatment	Ramp rates	0.1 to 1 C/min
	Set points	Every 10-20 C
	Hold times	8-12 hours

Discussion of Results after Heat Treatment of Capsules

Images of some of the formulations shown in Table-5 before and after heat treatment are shown in Figures10, 11,12,13,14,15,16,17,18,19,20,21,22,23. As indicated in Table-5, several of the samples either fused or fell apart on heat treatment in furnace. Only samples PII-34, PII-36, PII-39,and PII-57 remained intact and were selected for thermal cycling tests. The results for these are discussed in next section.

Table 5. Design of Experiments

RUN	Sample No	ICON	BCON	MIDDLE	OUTER	Comments
1	P-II-44	10	200%	6	19	Fused after heat treat
2	P-II-45	10	200%	6	29	good after heat treat
3	P-II-46	10	200%	10	24	fused after heat treat
4	P-II-47	10	200%	19	19	fused after heat treat
5	P-II-48	10	100%	6	19	fused after heat treat
6	P-II-49	10	100%	10	24	good after heat treat
7	P-II-50	10	100%	19	24	mostly broken after heat treat
8	P-II-34	10	100%	19	29	some cracked, good after heat treat
9	P-II-51	20	200%	6	24	fused after heat treat
10	P-II-52	20	200%	10	19	fused after heat treat

11	P-II-53	20	200%	19	24	mostly broken after heat treat
12	P-II-54	20	200%	19	29	good after heat treat
13	P-II-55	20	100%	6	24	fused after heat treat
14	P-II-41	20	100%	6	29	mostly broken after heat treat
15	P-II-56	20	100%	10	19	fused after heat treat
16	P-II-39	20	100%	10	29	mostly broken after heat t
17	P-II-57	20	100%	19	19	good after heat treat

ICON = Wt. % of Cloisite clay relative to kaolin
BCON = Ceramabind concentration; 100% is baseline formulation from Phase I
MIDDLE = Wt. % concentration of hydroxypropyl cellulose layer, relative to core.
OUTER = Wt. % of outer coating material relative to core; 29% is baseline formulation from Phase I

Some trends can be seen between formulation and performance of the capsules after heat treatment of the capsules to 340°C. For example, all of the capsules with only 19% outer coating were fused together. The observed fusion suggests leakage of the salt from within the capsule. As the capsules cool for imaging, the leaked salt acts as a binder to fuse the capsules to a solid mass at room temperature. Some of the 24% outer coated samples were fused, and none of the 29% outer coated samples were fused. For the middle layer, most of the samples were fused due to leaking salt. However, good samples were obtained with all three middle coating layers. No trend is evident from samples with varying ICON or BCON, as formulations with both variations of each parameter yielded good capsules.

Figure 10. PII-44 before and after treatment.

Figure 11. PII-45 before and after treatment.

Figure 12. PII-46 before and after treatment.

Figure 13. PII-47 before and after treatment.

Figure 14. PII-48 before and after treatment.

Figure 15. PII-49 before and after treatment.

Figure 16. PII-50 before and after treatment.

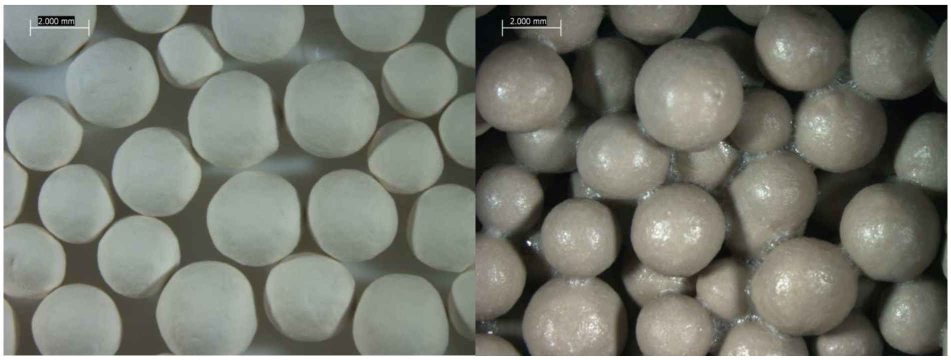

Figure 17. PII-51 before and after treatment.

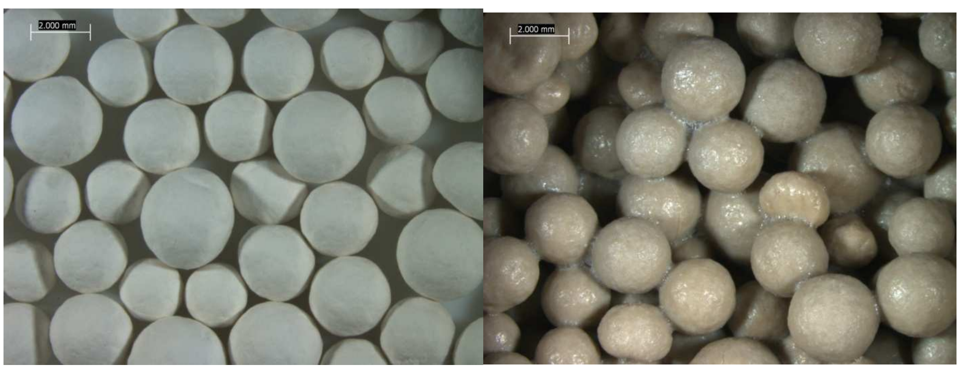

Figure 18. PII-52 before and after treatment.

Figure 19. PII-53 before and after treatment.

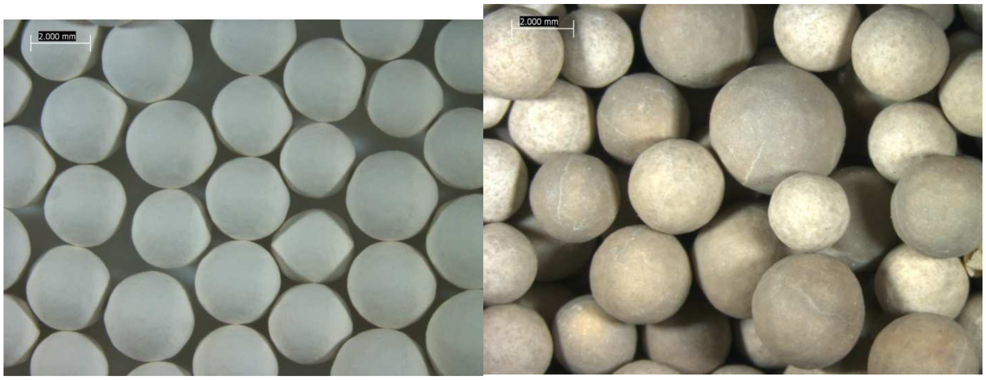

Figure 20. PII-54 before and after treatment.

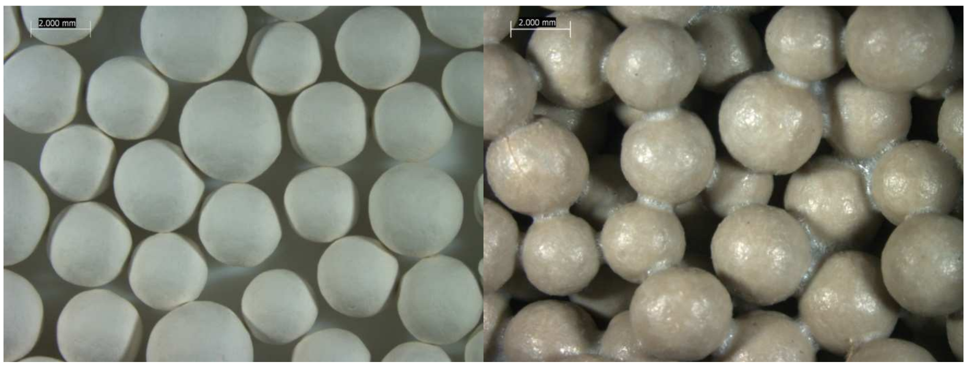

Figure 21. PII-55 before and after treatment.

Figure 22. PII-56 before and after treatment

Figure 23. PII-57 before and after treatment

TASK 2. THERMAL CYCLING TESTS –

Design of TerraDipper

A test rig was designed, developed and built for accelerated testing of the effect of thermal cycling on PCM capsules.

Functional Objectives:

1. Heat and cool the test capsules to the temperatures approximating field operating conditions.

2. Achieve maximum number of heat/cool cycle in the shortest time possible to complete the required number of test cycles.

3. The minimum time exposure time for capsules in hot environment is for the capsule to undergo complete melting of salt in the capsule and subsequent heating to high operating temperature. Similarly, the minimum exposure time in the cold environment is for the capsules to undergo complete freezing and cooling to cold operating temperature.

Design Requirements:

The most important design requirement was to meet the minimum heat/cool cycle time in the shortest time. Based on this consideration, and also to avoid pumping of heat transfer liquid and the associated complications, it was decided to use a hot tank / cold tank system with capsules dipped alternatively in each - hence the name “TerraDipper”.

- Automatic, unattended, continuous operation of the heat/cool cycles
- Adjustable temperature controls for the hot and cold tanks
- Adjustable timers to vary the soak times in each tank
- Option for manual operation, for loading and unloading of capsules into the holding trays
- Data logging to log the temperatures of the tanks and the salt trays as they are transferred from tank to tank
- Remote connectivity to check data logs in real time
- Remote notification if system parameters exceed or fall below specified limits
- Remote switch off facility to switch off the system in case of unsafe or undesirable operation.
- Modular, flexible design and assembly for quick, easy maintenance and modifications if required

System Description:

The system consists of a hot tank and a cold tank system into which the capsules are dipped alternatively to be heated and cooled, hence the name “TerraDipper”. Figure 24 shows a schematic of the TerraDipper.

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- Modular, flexible design and assembly for quick, easy maintenance and modifications if required

1. Two steel tanks 4” in diameter and 8” height connected by a 4” wide “gallery”

- One of the tanks is designated as a Hot Tank containing Heat Transfer Fluid (HTF) at a variable temperature of up to 500C.
- The second tank is the Cold Tank containing HTF at a variable temperature, typically at 250C (this is 80 C below the freezing temperature of PCM).
- The “gallery” is a passage way at the top of the tanks for the capsule trays as they are transported from one tank to the other. It provides containment for the spills of HTF, which would then flow into one of the tanks. HTF in both tanks is maintained at the same level up to the floor of the gallery. This ensures constant HTF volumes in both tanks despite any transfers or spills due to the movement of capsule trays from tank to tank.

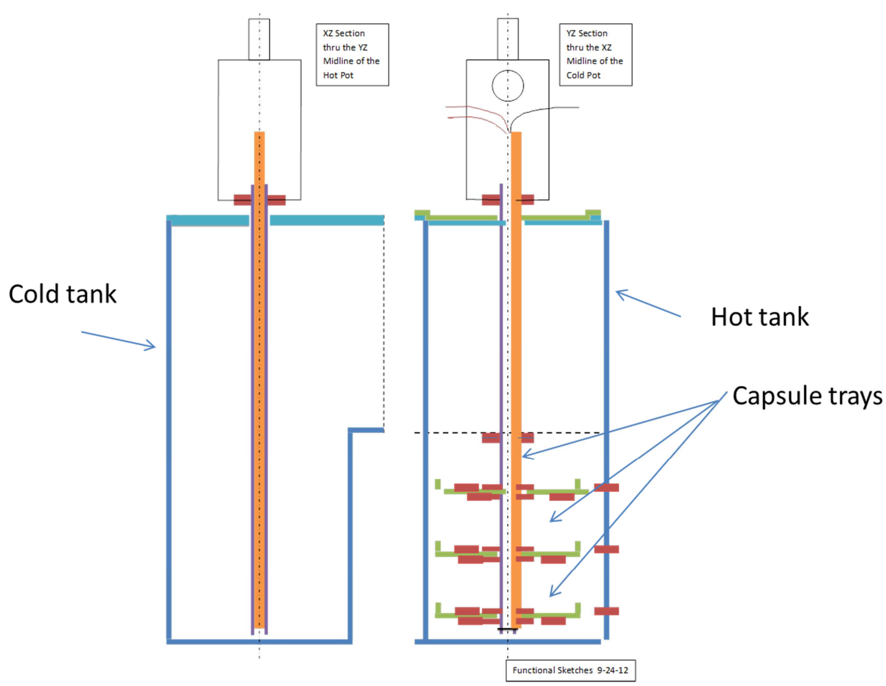


Figure 24 Schematic of the two-tank TerraDipper test setup

Figure 25 show the capsule trays and a SolidWorks drawing of TerraDipper.

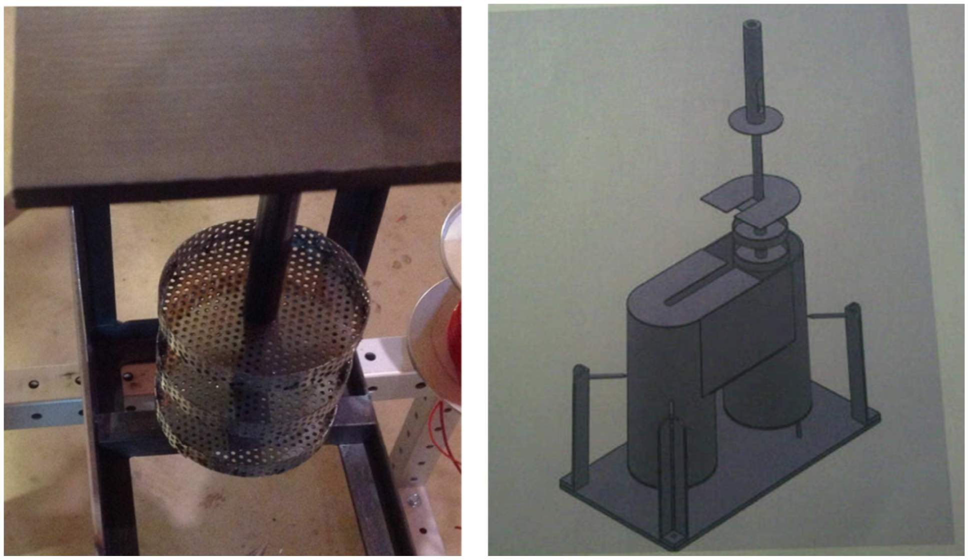


Figure 25 . (Left) Capsule trays (right) SolidWorks drawing of the TerraDipper

2. Heat Transfer Fluid (HTF)
   - HiTec salt mixture as the HTF to soak the capsule trays in the tanks for heating and cooling
3. Capsule Trays
   - Three 3-1/2” diameter perforated trays mounted on a central tubular stem designed for easy introduction and removal of test samples of PCM capsules
4. Movement Mechanism
   - One vertical electrically operated actuator with an adjustable stroke length of 12”, with provision for easy attachment of capsule tray assembly. This vertical actuator is mounted on a horizontal actuator.
   - One horizontal electrically operated actuator with an adjustable stroke length of 8”. The vertical actuator is mounted on this.
   - Mechanical stops to prevent overshoot of horizontal and vertical movements
5. Automated Movement Control System
   - Top and bottom Limit Switches to sense the position of the tray assembly as it moves up and down into the tanks
   - Hot side and Cold side limit switches to sense the position of the tray assembly as it moves from tank to tank
   - Two adjustable electronic Timers, one for each tank, to set the soak/dwell times for the capsule trays
   - Relay logic based control system for automatic and manual control of actuators for the vertical lifting and horizontal movement of cable tray assembly from tank to tank
6. Heaters, Sensors and Temperature Control

- Two high temperature Band Heaters on each tank
- Bolt-on RTDs on the tanks and the gallery
- RTD probe in the capsule tray wired through the tubular stem
- Omega 1/8 DIN fuzzy logic Temperature Controllers one for each tank
- Heater Power and Control system, with protective circuit breakers and fuses.

7. Data Logging

- 4 channel Data Logger
- A dedicated PC connected to the data logger to continuously log temperatures
- Cellular data based wireless hot spot providing always-on Internet connectivity to the PC
- Software for remote monitoring of logged data in real time over the Internet
- Software to send email alerts in case of pre-set alarm conditions

8. Remote Shut-off Facility

- On-off controller for control circuit power supply, connected via Wi-Fi to the dedicated cellular internet hotspot
- Software apps on smart phones and tablets to remotely connect over the internet to the controller, enabling shutting down the system in case of abnormal operation observed or notified via/by the data logger

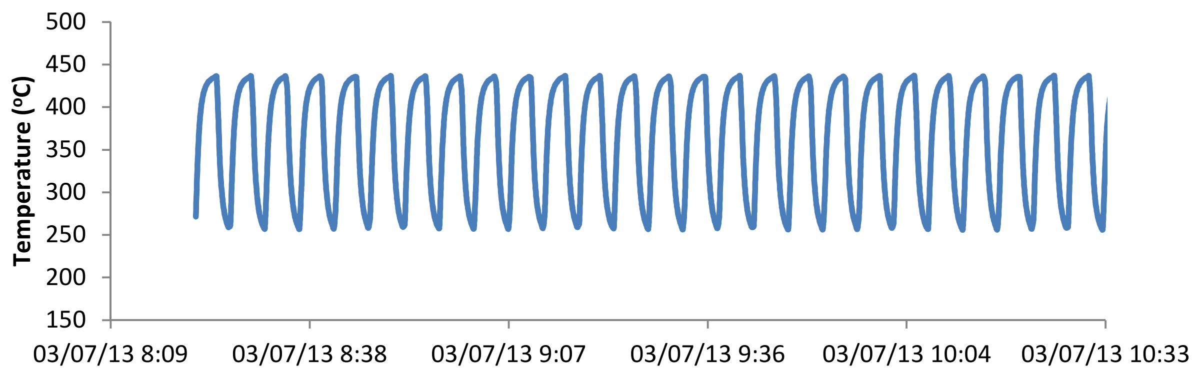


Figure 26 TerraDipper probe temperature.

Figure 26 shows a sample of the oscillating sample tray temperature probe data as it is exposed to the two tanks with 5 minute intervals. The control box and laptop for data collection are shown in the left image of Figure 27. The robotic arm and insulated tanks are shown in the right image. The samples are cycled from 250 °C to 430 °C for this example. The temperatures and cycle times can be adjusted. The current temperatures and cycle times are sufficient for phase change of the encapsulated KNO_3.

Figure 27 Front and back of TerraDipper. Capsule trays on linear actuator shown on right of picture

Hot design requirement is to heat to 600C. However, HiTec salt degrades in open environment above 500C. The test rig with closed environment with nitrogen blanket will be expensive and difficult to manage. Tests at 600 C temperature are conducted in the DSC or TGA.

The TerraDipper system is designed to expose phase change material capsules to alternating cool (230-250 °C) and hot (400-450 °C) molten salt environments. Through the use of separate molten salt tanks, and robotic arm carries the sample between the two baths every 4 to 5 minutes, depending upon the timing set for the mechanical movement. Calculations show the salt in the salt in the capsule changes phase in 2 to 3 minutes in the bath.

Results of Tests in TerraDipper for Selected Capsules:

Formulations tested with the TerraDipper are shown in **Error! Not a valid bookmark self-reference.**. The initial samples tested with the TerraDipper were PII-34 and PII-36. Both samples were first treated to 450 °C and then cycled 600 times between 250 °C and 430 °C. Sample PII-36 completely fell apart. Sample PII-34 appeared intact, but upon further inspection all capsules were cracked. Images of PII-34 before and after cycling are shown in Figure 27. The smaller brown capsule in the right image is the remnant of a core inner layer, which is also composed of clay. Additional subsequent samples tested include PII-39 and PII-41. Only ten capsules were tested for a 250 cycle experiment. All of PII-41 fell apart while a few of PII-39 remained intact. Images of the intact samples and their cross section are shown in Figure 28. It is evident in the upper cross section image that the encapsulated salt is still present, seen as the white inner ring within the capsule core. It is more difficult to identify a salt layer in the lower electron micrographs of the same sample.

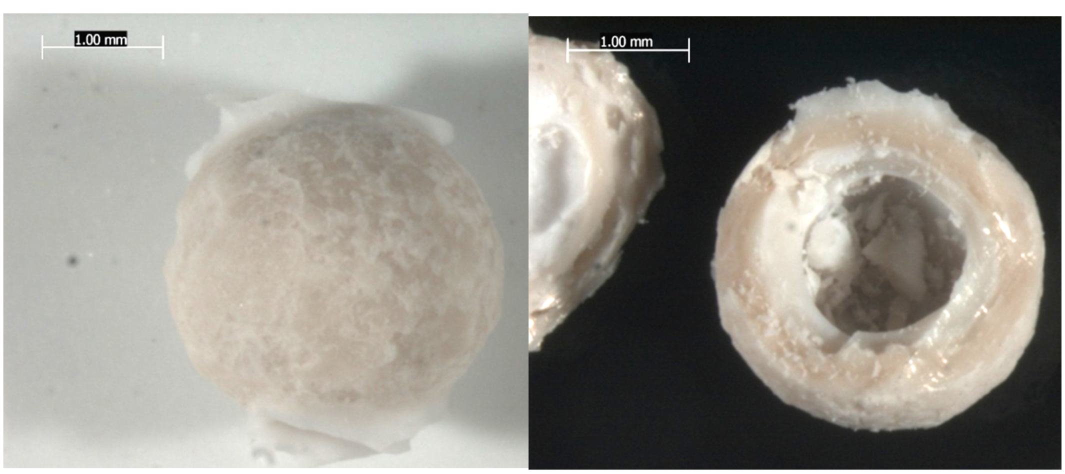
Table 6. TerraDipper Tested Formulations

Sample	Description	450°C Treatment Results
PII-34	10:90 New clay to kaolin, HPC middle	Intact, few cracks
PII-36	20:80 New clay to kaolin, HPC middle	Intact
PII-39	10:90 New clay to kaolin, 1/3 HPC middle	Half survived
PII-41	10:90 New clay to kaolin, ½ HPC middle	Intact, few ruptured

Figure 27. Sample PII-34 before and after 600 cycles in TerraDipper.

While initial tests with the TerraDipper yielded poor results for capsule durability. Most of the capsules broke when they were taken out from the sample holders. The sample holders for the capsules were manually molded wire cages that applied stress onto the capsules once cooled and dried with the residual molten salt bath material. New sample holders were redesigned and tests will be conducted again.

Specially designed and fabricated sample boxes, shown in Figure 29, were used to contain the capsules during the cycling experiment. While the use of the new sample cages simplified the addition and removal of the capsules from the TerraDipper system, the isolation of the capsules for inspection was still complicated by the solidification of the tank salt around the samples.



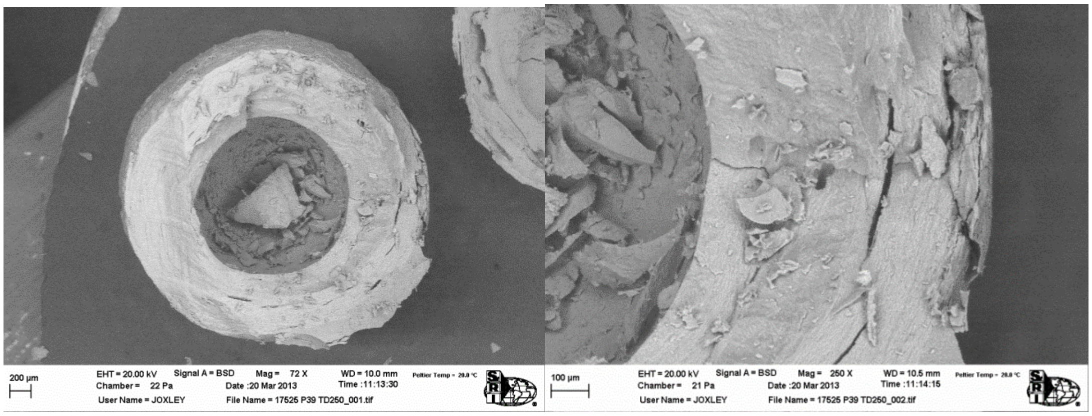


Figure 28. PII-39 after 250 TerraDipper cycles.

Using cages similar to those shown in Figure 29, sample PII-57 was exposed to 1000 cycles in the TerraDipper system. All capsules survived the prolonged exposure to temperature cycling. Optical and electron micrographs of the capsule cross sections are shown in Figure . The inner salt core is visible and distinct from the outer clay shell. Similar to other sample, the salt refreezes along the inner wall of the capsule.

Upon closer inspection of the shell for sample PII-57 after 1000 cycles, some changes are evident. Optical and electron micrographs of the shell are shown in

Figure . The optical micrographs show white lines within the clay shell that are not present in the sample immediately following preparation. It is presumed that the white lines are salt, however it is unclear if the salt is from the core or shell material. Regardless, the presence of salt in the shell is indicative of potential diffusion of salt through the shell wall. Salt diffusion will decrease the life and performance of the capsules as the inner higher melting salt is depleted or diluted by the outer lower melting salt. Further evident of the intrusion is seen in the lower right image of

Figure . A porous network is visible that was also not present in the initial capsule shell wall, providing further evidence for breach of the shell.

Figure 29. Photograph of the TerraDipper sample cages.

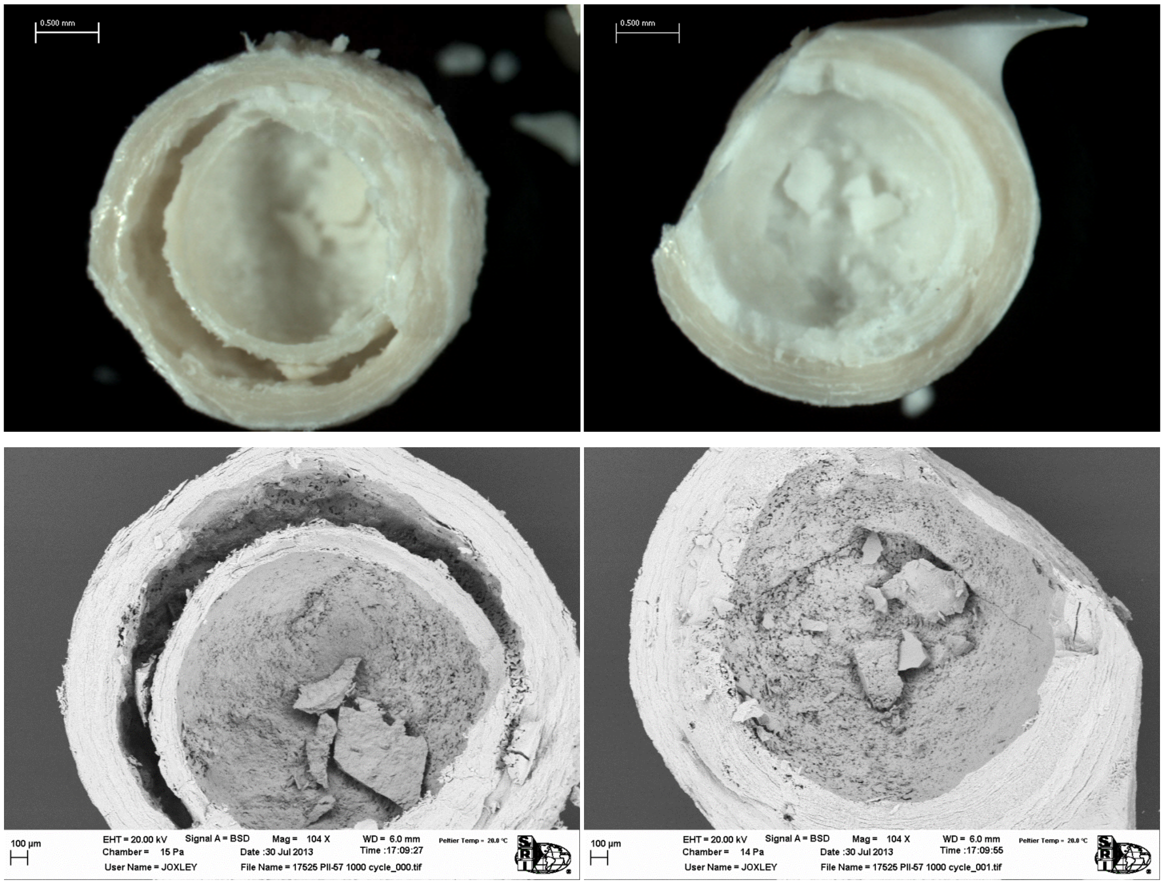


Figure 30. Optical and electron micrographs of sample PII-57 after 1000 cycles in the TerraDipper.

Overcoating with Nickel

Capsules so far have been cycled in DSC and TGA and survived several cycles. The real test will be whether capsules will survive in hot molten salt heat transfer fluid. Since the capsule shell is porous, we also investigated adding another layer of coating of Nickel using the Nickel carbonyl process. This process is conducted at 170^{o}C and a thin layer of metal coating can help to seal the pores.

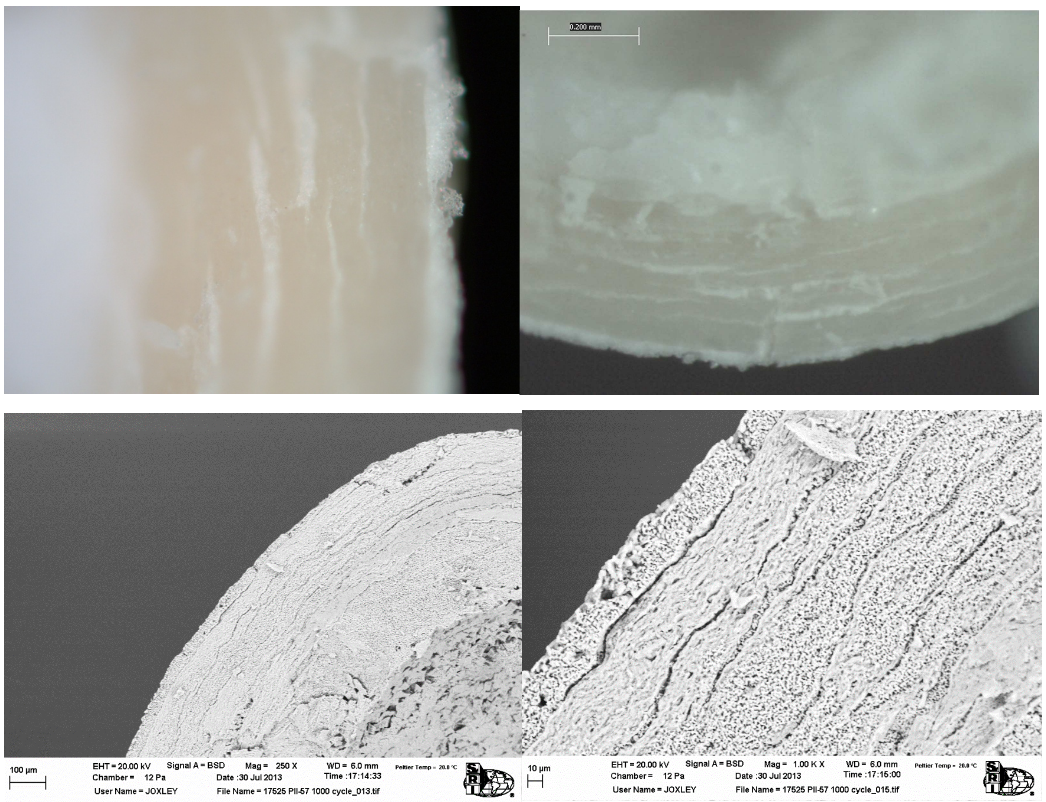


Figure 31. Optical and electron micrographs of capsule shell for sample PII-57 after 1000 cycles in the TerraDipper.

In an effort to strengthen the current capsules and improve barrier properties, a sample of PII-36 was coated with nickel. The target coating thickness was 5 µm. While this is insufficient to significantly increase mechanical integrity, it is suitable to introduce additional barrier properties. Electron micrographs for the capsules are shown in Figure . The surface of the bead, shown in the upper images, is rough and there are indications of pore formation and incomplete coating. The lower images show cross sections of the shell. The shell thickness is at most 5 µm, and was observed to be less than 1 µm in many places. Based on the observation of porosity, it is presumed that the barrier properties will not be present unless and thicker more continuous coating is applied.

Despite the inhomogeneity of the coating, the sample was subjected to elevated temperatures dry and submerged in HiTec molten salt. Optical micrographs of the sample before and after thermal exposure are shown in Figure . As received, show in the upper left image, the capsules have an appearance that is consistent with a nickel coating.

Following dry exposure to 350 °C, the capsules are iridescent with shades of blue, purple and orange, shown in the upper right image. The capsules all appear to be intact.

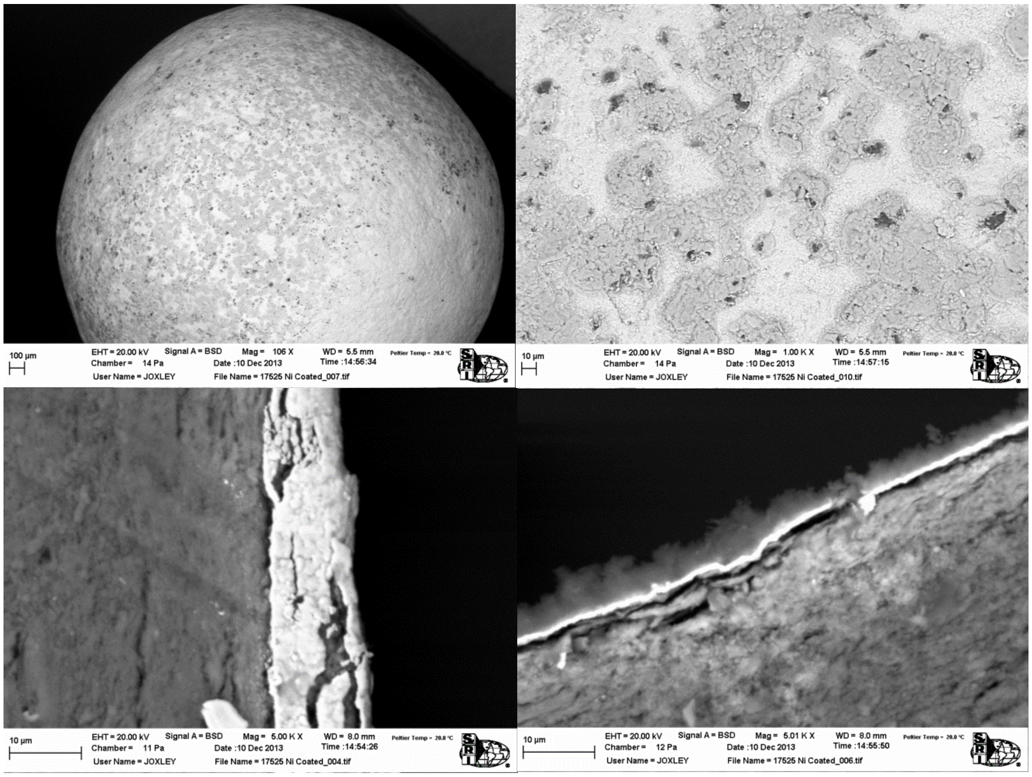


Figure 32. Electron micrographs of sample PII-36 coated with nickel.

Figure 33. Optical micrographs of nickel coated PII-36 after heating to 350 °C

When exposed to molten HiTec salt, 60% of the capsules fell apart and those that survived are shown in Figure 34 to be cracked. This may be due to the thermal expansion of the metal shell, or the capsule itself. The capsules were heated to 310 °C over 12 hours, and then to 350 °C over 2 hrs. A thicker and more homogeneous coating may provide more mechanical stability.

Figure 34. Optical micrographs of nickel coated PII-36 after heating to 350 °C in HiTec salt

Measurements to Test for Integrity of Capsules

To test if the capsules are robust or if any changes in properties of capsule or salt has occurred or to examine the physical changes to the capsule as it is thermally cycled, following measurements were taken periodically:

- Texture analyzer to measure hardness
- SEM to examine microstructure of shell outside and cut-open
- Optical microscopy to look for any visible cracks
- DSC to measure change in heat of fusion
- TGA to measure if the capsule is losing weight due to material escaping
- Cyclic voltammetry to test for corrosiveness of HTF due to contamination with ruptured capsules

As capsules rupture, small particles of clay or shell material may contaminate the HTF which can cause damage to pump and erosion to pipes. Since this is difficult to emulate in a laboratory, it is best to conduct these tests in Phase 3 when a scaled model of TES is built. Other properties that may be of interest are changes in thermal conductivity and specific heat due to contamination of HTF with the selected salt inside the capsule. These tests can be conducted once the salts are selected for the CSP. KNO_3 salt currently used in the capsule does not alter the properties of the HiTec salt which is a mixture of sodium, potassium nitrate and sodium nitrite. Hence these tests were not conducted.

An important test to characterize for the integrity and robustness of capsule is a hardness test. This test was conducted with salt prills, raw capsule, heat treated capsule and will be conducted periodically after thermal cycles. To conduct these tests a microcapsule mechanical strength was initially quantified using a TA-XT Plus Texture Analyzer from Texture Technologies Corp.

summarizes the values observed for initial cracking and mechanical failure of a neat KNO_3 prill, untreated capsules, and heat treated capsules. Figure graphs the data for comparing the KNO_3 core material to untreated and heat treated capsules. Of the formulations tested, most retain the mechanical strength of the neat core material that had an initial mechanical failure at 13.8 N. The original Cloisite clay shell, sample PII-29, showed the greatest strength. It is also clear from the difference in the heat treated samples for PII-34 and PII-36 that an increase in clay concentration also contributes to mechanical strength. As expected, heat treatment and removal of the sacrificial layer weakens the capsules. For sample PII-36, the rupture force is decreased from 29.8 N to 19.5 N, which is still stronger than the neat KNO_3 prill. However, some initial cracking is observed at 7-10 N, evident in the slope change for the PII-36 450C curve in Figure . An increase in clay concentration may mitigate the initial weakness observed in the heat treated sample.

Table 7. Rupture Force Testing

Sample	Crushing Force (N)*	Comments
KNO_3 Prill	13.8 ± 1.8	
PII-29	45.2	Original clay shell
PII-36	29.8 ± 4.9	Kaolin shell with 20% original clay
PII-34 450C	5.94 ± 1.33	Kaolin shell with 10% original clay
PII-36 450C	19.5 ± 3.8	Some fluctuations at ~7-10 N

*at least three samples tested

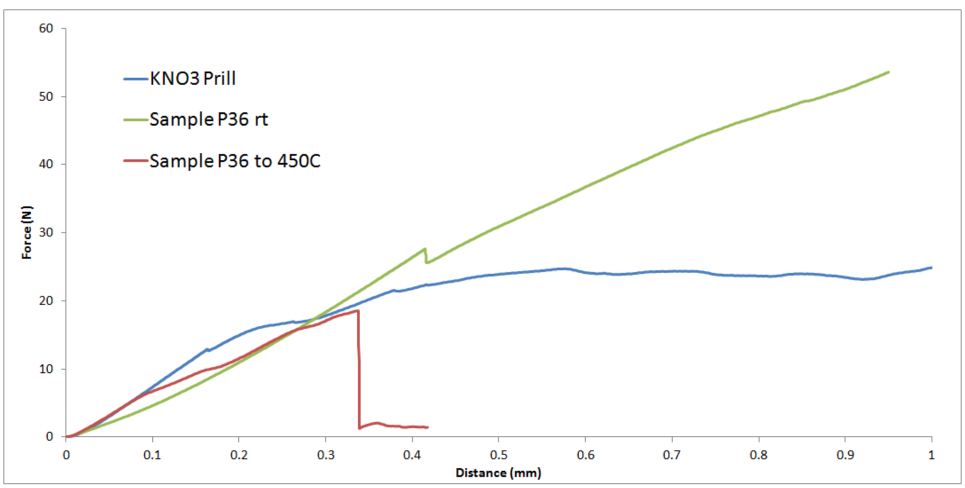


Figure 35 Rupture strength testing of microcapsules.

Prediction of Failure Rates Using Statistical Methods

Survival Analysis

Survival analysis techniques, such as proposed by Kaplan-Meir and /or Cox are used to compare the risks for capsules from different designed recipes rupturing due to thermal cycling over time. If a crack is observed in an optical microscope, then the capsule is deemed as ruptured. Using the seventeen designed recipes, only the capsules from the recipes that survived the heat treatment are used. In measuring survival time, the start and end-points are defined as the beginning of a periodic cycle and end of the cycle and the censored observations are noted. The periodicity is selected as 10 cycles when the capsules are fresh. The periodicity is changed to 250 cycles after the first 100 cycles and to 1000 cycles after the first 1000 thermal cycles are complete. The thermal cycle tests are terminated after 10,000 cycles. Overall 20 observations are made.

Kaplan–Meier provides a method for estimating the survival curve, the log rank test provides a statistical comparison of two groups, and Cox's proportional hazards model allows additional covariates to be included. Both of the latter two methods assume that the hazard ratio comparing two groups is constant over time.

Hardness tests of capsules are conducted at beginning and end of thermal cycling experiments to evaluate the robustness of capsules that survived. The recipe that produced the robust capsules is deemed the golden recipe.

Estimating survival curve
The survival function, S(t) is defined as the probability of surviving or capsule staying intact to time t. The hazard function, h(t) is conditional probability of rupturing at time t having survived to that time.

$S(k) = p_1 * p_2 * p_3 * \ldots * p_k$

$p_i = (r_i - d_i) / d_i$

p_k is the probability of surviving to period k, r_i is the number survived, and d_i is the number ruptured. A plot of S(t) vs t is the survival curve.

A portion of the capsules from each batch is thermally cycled in the TerraDipper. After each of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 250, 500, 750, 1000, 2000, 3000, 4000, 5000, 7500 and 10000 cycles the capsules are taken out from the sample holder in the TerraDipper, dried of the HiTec salt on the capsules and examined for cracks in the optical microscope and the survivors counted and recorded. Capsule with a crack is considered as ruptured. At the beginning and at end the cycles a capsule tested for hardness for each batch. The hardness test is a destructive test and the capsule is considered to be representative of the batch.

For recipes with high probability of survival, a comparative survival analysis using log rank test is conducted.

Note: The Cox proportional hazards model is very important as it will model the hazard function in terms of time and temperature as well as the important factors identified in the design of experiment. Also included in the model could be the modes of failure. We then would be able to fit the model and find its minimum, and set thresholds on the hazard function. When completed, we would have a linear equation for the hazard function, and should be able to test for the significance of the factors, at the values of each layer as well as at the required time and temperature of the test.

TASK 3: MAKE LARGE CAPSULES (APPROX 10 MM) USING TABLETING AND PAN COATING METHOD

In addition to continuing work on the 2-5 mm KNO_3 prills, a similar approach was applied to larger 10-15 mm capsules (beadlets). Mathematical model suggests ~10mm capsule size is the economic optimization for thermal storage. A tableting method was used to make the beadlets as described below.

Beadlet Formation

The first step in this process was the preparation of a salt core for coating. Potassium nitrate is not commercially available in uniform bead sizes of 10-15 mm, therefore beads have to be prepared. Methods considered included casting from molten salt or compression of dry salt powder. Given the resources at SwRI, compression was determined to be the best solution. Initial formulations were tested using a tablet press. Potassium nitrate powder was pressed into a numerous pellet formulations using different sacrificial binders to adjust porosity and surface morphology. The goal was to produce a tablet with sufficient porosity to accommodate expansion after coating of the tablet and subsequent phase change to a molten core. Representative images are shown below in Figure .

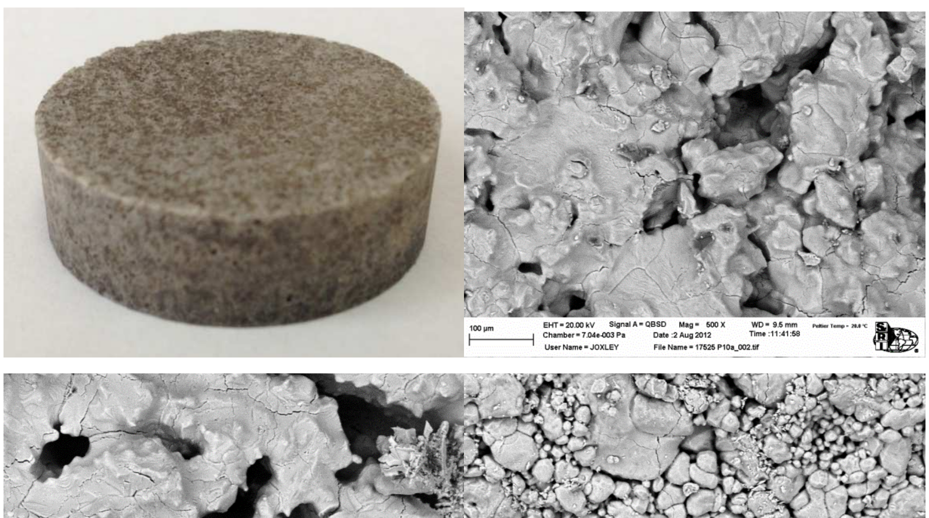


Figure 36. Optical micrograph of 1 inch heat treated potassium nitrate tablet (upper left), electron micrographs of tablet surface at 500x with three different binders: palmitic acid (upper right), stearic acid (lower left), polyethylene glycol (lower right).

The porosity was calculated based on the density calculated from weight and volume measurements. A summary of the data from various formulations is shown in Table 8. Tablet Formulations and Porosity Measurement, Heat Treated 24 hours at 250 °C. The porosity in all cases is sufficient to accommodate the expansion of the potassium nitrate salt after melting. The best formulations were C and H, which correspond to the use of ethyl cellulose and an 80:20 ratio of ethyl cellulose/polyethylene glycol, respectively.

The sample tablets prepared above were larger than the target 10-15 mm size range, and too large to coat using a standard pan coating process. Therefore, a tablet press is used to prepare larger quantities of smaller tablets similar in size and shape to tablets used in over-the-counter pharmaceuticals. Commonly used for tableting of pharmaceuticals, tableting machines are capable of high throughput compression of dry powders into tablets. The tablet press was setup to run potassium nitrate powder using a Zpy-15 Rotary Tablet Press and a die set for tablets with a diameter of 1 cm and height of 1.25 cm. Images of the tablets are shown in Figure 37. The tablets are cylindrical with domed ends. These tables were run without the additives or pore formers.

The porosity of the pellets was measured through volume and mass analysis. Physical measurements were made for a sample of 25 pellets, combined with the weight of pellets and consideration of the density for potassium nitrate. After heat treatment at 315 °C for 12 hours, the porosity of the tablets is 20-21% despite the absence of pore forming ingredients. Electron micrographs in Figure of the tablet surface show the pores present between the compacted potassium nitrate particles.

Table 8. Tablet Formulations and Porosity Measurement, Heat Treated 24 hours at 250 °C

	Mass	Height (cm)	Radius (cm)	Volume	Density	%Porosity	$T_{porosity}$*	$\Delta_{porosity}$
A	8.8081	0.99	1.2945	5.212	1.690	19.90%	22.35%	2.44%
B	6.43	0.82	1.296	4.327	1.486	29.57%	25.94%	-3.63%
C	5.699	0.743	1.29	3.884	1.467	30.47%	25.88%	-4.59%
D	5.315	0.673	1.2795	3.461	1.536	27.23%	24.80%	-2.42%
E	7.715	0.916	1.28	4.715	1.636	22.45%	22.05%	-0.40%
F	6.641	0.817	1.28	4.205	1.579	25.16%	24.16%	-1.00%
G	5.795	0.738	1.282	3.811	1.521	27.92%	25.59%	-2.33%
H	6.108	0.81	1.293	4.254	1.436	31.96%	24.16%	-7.80%
I	6.368	0.789	1.29	4.125	1.544	26.83%	24.26%	-2.57%
J	6.49	0.814	1.293	4.275	1.518	28.06%	22.85%	-5.20%

Figure 37 Potassium nitrate pellets made with tableting press.

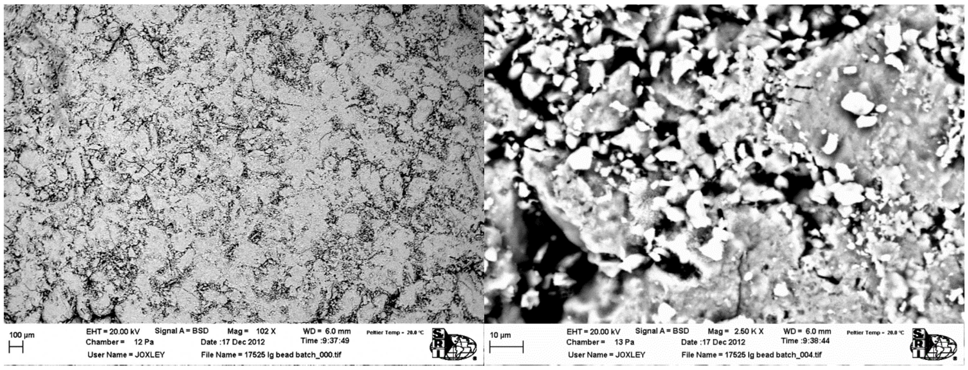


Figure 38. Electron micrographs of potassium nitrate tablet surface.

Beadlet Overcoating

Beadlets were overcoated using a modified benchtop pan coater, shown in Figure 39. A pan coater is an angled spinning drum. As granular material tumbles in the drum, a mixture of coating material is sprayed into the chamber to coat the granules. Heat and ventilation are applied externally to enhance drying and curing of the coating. This process is used widely in the pharmaceutical and confectionary industry for coating tablets and candies, respectively. The pan coater rolls the beadlets at a low speed, less than 60 rpm, while a coating material is spray onto the tumbling beadlets. The system is purged with warm nitrogen to evaporate the coating solvent.

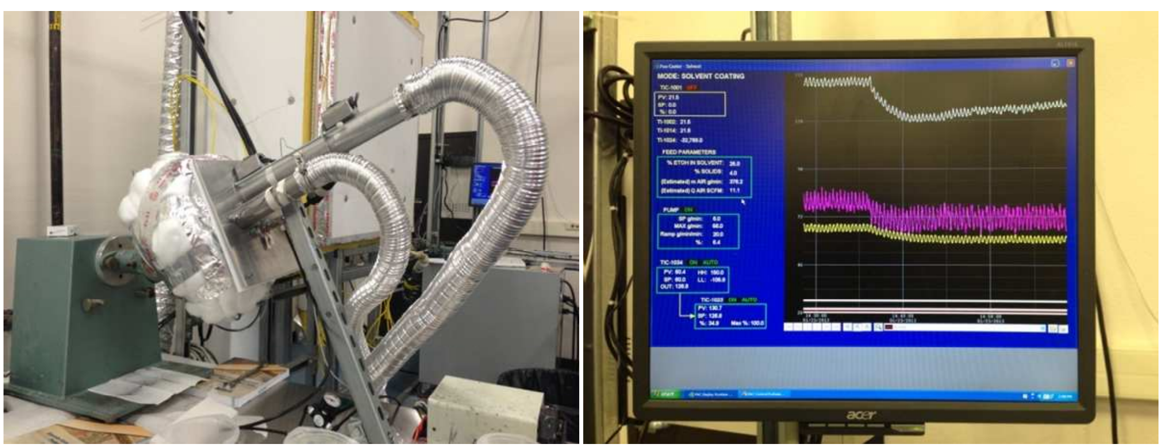


Figure 39. Pan coating system.

A summary of the tested coatings is listed in Table 9. The initial beadlet coating focused on the use of the original Cloisite Na+ coating developed in Phase I. Electron micrographs of the beadlet surface before and after coating are shown in Figure . The surface morphology is smoother as the coating material seals the surface voids on the beadlet. Further evidence of the coating is shown in the right image of Figure , where the coating layer is visible in the upper portion of the cross sectioned beadlet. The left images show the porous morphology of the KNO_3 is retained within the center of the beadlet.

Table 9. Tablet Overcoating Formulations

Sample	Coating
P44	Cloisite Na+ capsule coating
P45	PII-36 coating
P46	PII-36 coating, with 3x ethyl cellulose
P47	P46 coating, with clay reduced to 2%

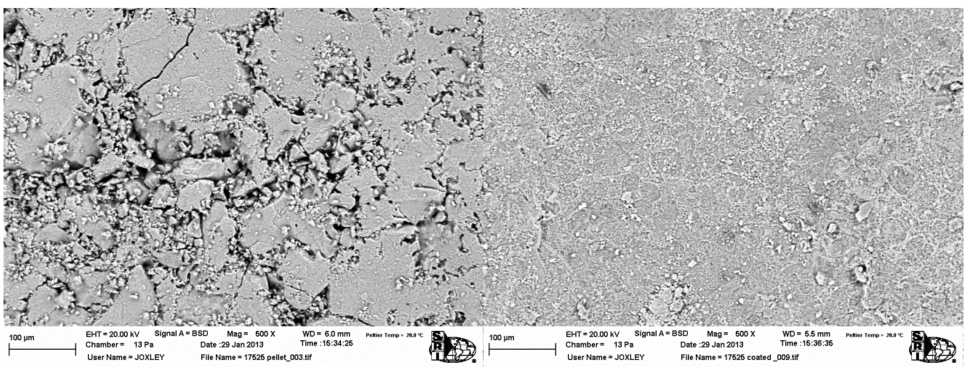


Figure 40. Sample P44 before and after coating.

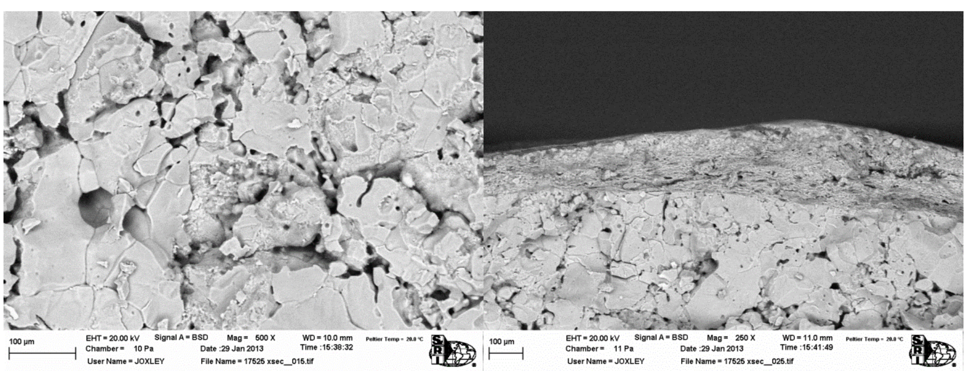


Figure 41. Sample P44 cross section after coating.

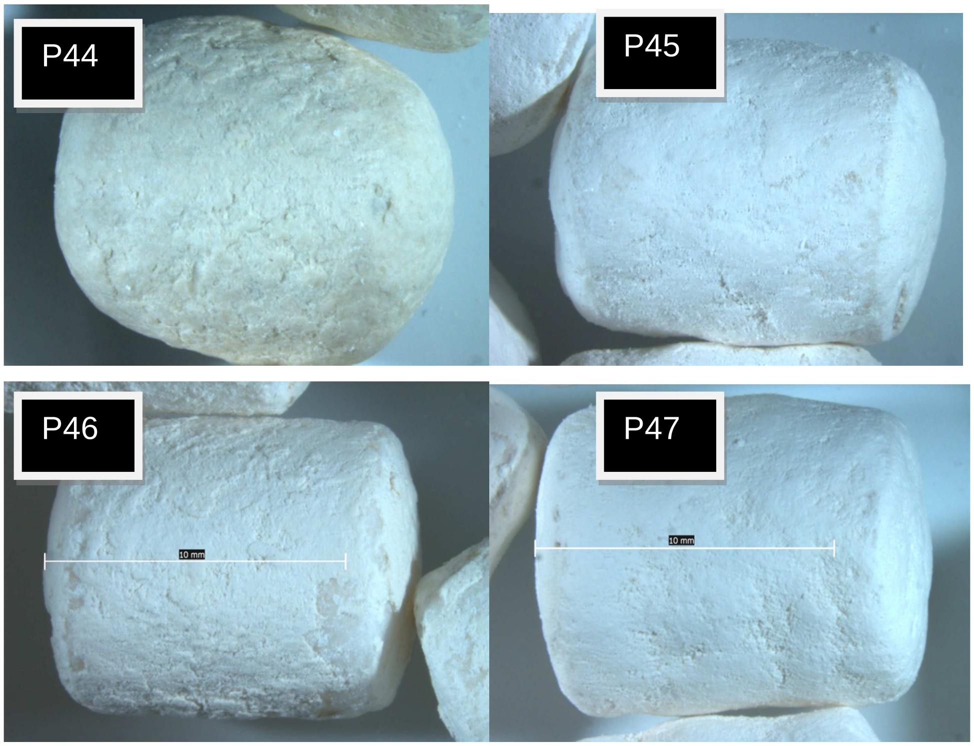


Figure 42. Overcoated beadlets.

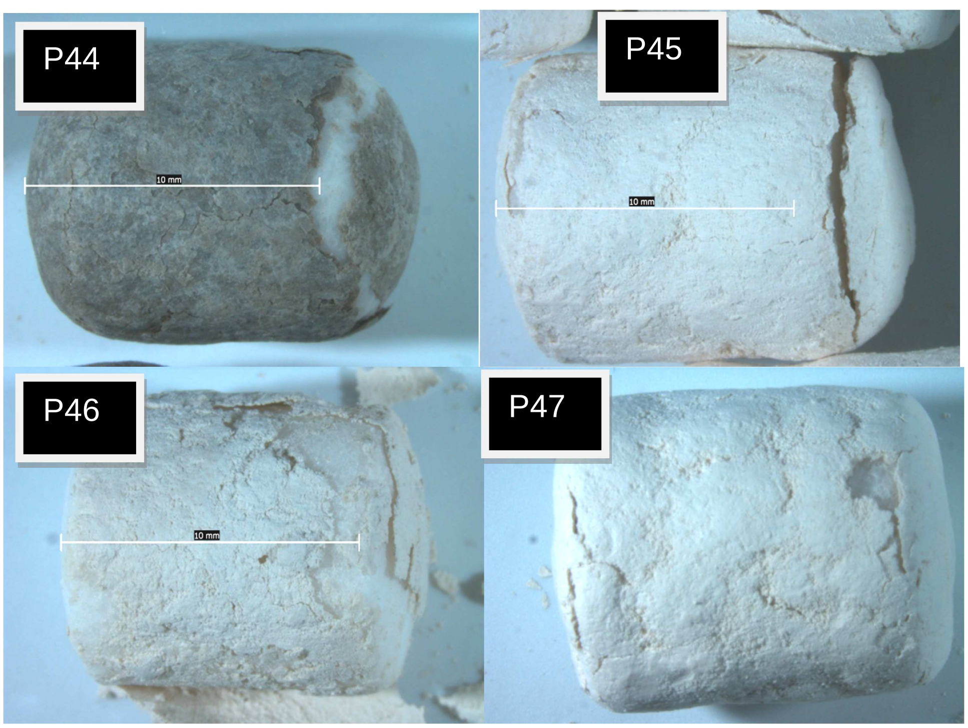


Figure 42. Overcoated beadlets after heat treatment to 315 °C.

Images of the overcoated beadlets are shown in Figure . The initial tablet shape for the core in sample P44 was lost during coating. Due the low solids content of the coating solution, the coating time was over 24 hours to achieve a 10% by weight coating. The long processing and tumbling time slowly erodes the edges of the beadlet, resulting in a more round beadlet and thin, or lack of, coating at the edges of the beadlet. Due to this observation, the use of kaolin was employed to increase the coating solids content and reduce the coating time to several hours. The result, seen in sample P45, is a better retention of shape and slightly smoother coating. In an effort to smooth the coating further, similar to coatings observed on commercially available pharmaceutical tables, the ethyl cellulose film former content was increased and the Cloisite Na+ decreased to further increase the solids concentration. While the final sample, P47, has a noticeably smoother coating, the surface irregularities remain a concern.

Similar to the microcapsule studies, the tablets were heat treated to 315 °C to remove the ethyl cellulose binder and cure the coating. As seen in Figure , all of the coatings failed. There are multiple reasons for this failure. First, all of the failure occurs at the edge formed by the tableting process. The edge is the thinnest coating spot due to erosion from the pan coating tumbling process. Second, the coating consistency remains rough. The result is a flaky patchwork coating rather than a smooth continuous coating. Finally, further analysis of the core beadlets used for overcoating show that their porosity was lost during scale-up, resulting in beadlets with no void space for expansion.

Due to problems encountered with coating quality, bead quality, and available resources, beadlet production testing was suspended. Coating quality remained poor due to poor film formation and lengthy coating times that resulted in beadlet and coating abrasion. Bead quality and porosity was inconsistent when repeating the tableting procedure with a new batch of KNO_3 powder, which will require re-evaluation of the process parameters to generate porous beads. Finally, remaining funds and resources were allocated toward the completion of the smaller capsule experiments for TerraDipper testing.

TASK 4 ECONOMIC ANALYSIS OF EPCM

Comparing Costs of Encapsulated Packed Bed TES and Two-Tank TES

A comparative cost analysis of an EPCM-TES with a two-tank sensible heat TES using molten salt show the specific costs are significantly lower. The specific costs for EPCM are closer to the SunShot goal of $15 per kWh(t) stored. Table-12 shows a detailed breakdown of costs and the assumptions to arrive at these costs for the two TES systems. The second column in the table shows the baseline specific component cost used to estimate the cost for the selected TES system. Even though the real costs of the TES depend on site, location and availability of material, the analysis is important for comparing costs for *relative costs and reduction in cost of* the EPCM-TES system compared to the conventional two-tank system.

Table 10 . Comparison of Costs for EPCM-TES and Two-Tank TES

		Two-tank TES	***TerraCaps* PCM TES**
Storage Capacity	MWh(t)	3500	3500
Volume	m3	18519	11966
Operating Temperatures, Hot /Cold	deg C	560 / 280	560 / 280
Specific Heat HTF Salt	kJ/kg-K	1.5	1.5
Latent Heat	kJ/kg	0	220
Storage Effectiveness	%	90%	80%
Tank ID	m	39	32
Tank Ht	m	15.2	15.2
Surface Area/ tank	m2	4252	3137
Foundation Area /tank	m2	1195	804
Tankage			
Foundations, $/m2	$1,199	$2,864,628.27	$964,293.02
Platforms & Steel, $/m2	$292	$697,640.91	$915,877.30
Hot Storage Tank (SS), $/m2	$6,332	$26,920,607.78	$19,860,736.58
Cold Storage Tank (CS), $/m2	$3,799	$16,151,514.37	$ -
Distributors and additional Tank costs	est.	$ -	$1,000,000
Tank Insulation, $/m2	$206	$1,751,625.14	$646,132.62
Tankage subtotal		*$48,386,016*	*$23,387,040*
Tankage Specific Cost	*$/kWh(t)*	*$13.82*	*$6.68*
Balance of Plant (BOP)			
Surge Tanks	est.	$550,000	$550,000
Pumps & PCE	est.	$9,100,000	$9,100,000
Salt Melting System	est.	$2,040,000	$1,040,000
Interconnecting Piping & Valves	est.	$1,400,000	$1,400,000
Electrical	est.	$480,000	$480,000
Instrumentation & Controls	est.	$700,000	$1,050,000
Balance of Plant subtotal	*$*	*$14,270,000*	*$13,620,000*
BOP Specific cost	*$/kWh(t)*	*$4.08*	*$3.89*
Storage Media			
Capsule processing (est.)	$0.15/kg	-	$2,423,077
Salt	$1/kg	$33,333,333	$21,538,462
Energy for Salt Melting	est.	$145,000	$145,000
Media subtotal		*$33,478,333*	*$24,106,539*
Media Specific Cost	*$/kWh(t)*	*$9.57*	*$7.12*
TES Direct Costs Total		$96,134,349	$61,113,578
TES Direct Cost	$/kWh(t)	$27.47	$17.34
Engineering - (3% of direct)	3%	$3,124,559	$1,820,665
TOTAL	$	$99,258,908	$62,934,243
Total TES Installed Cost	$/kWh(t)	$28.36	$17.98

Section 5 Conclusions

Using encapsulated phase change materials is perhaps the best method for storing latent and sensible energy because design heat rates can be sustained throughout the charge and discharge process while using over 90% of the latent heat of fusion. This latent heat, in addition to sensible heat increased the energy density by over 50%, thus requiring 40% less salt and over 60% less capsule container. Therefore, the cost to store high-temperature thermal energy collected in a concentrating solar power plant will be reduced by about 40% or more, as compared to conventional two-tank, sensible-only storage systems. The cost for thermal energy storage (TES) system is expected to achieve the Sun Shot goal of $15 per kWh(t).

By encapsulating PCM in small capsules using a patented “Sacrificial-Layer” method, Terrafore has successfully demonstrated and optimized the manufacturing of capsules containing phase-changing inorganic salts. By using these capsules, we have increased the heat transfer area per unit volume of salt and brought the heat transfer fluid in direct contact with the capsules. These two improvements have increased the heat transfer coefficient and boosted heat transfer.

The program was successful in overcoming the phenomenon of melt expansion in the capsules, which requires the creation of open volume in the capsules or shell to allow for expansion of the molten salt on melting and is heated above its melting point to 550°C. We have demonstrated the process with a commonly used inorganic nitrate salt in a low-cost shell material that can withstand over 5,000 high-temperature thermal cycles between 250°C and 450°C. The shell used to encapsulate the salt was demonstrated to be compatible with a nitrate based molten salt heat transfer fluid typically used in CSP plants to temperatures up to 600 °C and withstood over 5000 thermal cycles between 250°C and 450°C

Even though the capsules remain intact, tests indicated that the “HiTec” salt entrained through the pores of capsules. Program constraints did not permit the further refinement of the recipe, so as to ensure capsule longevity to 10,000 thermal cycles, by eliminating the capsule pores entrainment. Nevertheless, by depositing a 5 µm nickel coating on the capsule, the pores were effectively sealed. Future tests must test the efficacy of the sealing method employed.

The above findings have led to the concept of a cascaded arrangement for storing heat in a single tank. Salts with different melting points can be encapsulated using the same recipe and contained in a packed bed by cascading the salt melting at higher melting point at the top over the salt melting at lower melting point towards the bottom of the tank. Mathematical models showed that with cascaded arrangement using three different salts in 10 mm diameter capsules, over 90% of the latent heat of fusion of salts and their sensible heats can be used. The cost of the encapsulated TES using three salts is estimated to be $17.98 per kWh using the technology developed here and the currently available components. Improvements in specific heat of heat transfer fluids, underway elsewhere, will reduce the cost to less than the SunShot goal of $15 per kWh(t).

A “tableting” method is used to make 10mm to 15mm capsules, which were termed as “beadlets”. Using this method, large batches of capsules can be produced quickly. It also significantly reduces the heat-treatment time, as the tablets possess adequate porosity or void volume. Porous “beadlets” cores were successfully prepared through the compression and “tableting” of KNO_3 powder. A pan-coating method was used to overcoat the tablets with same shells used in the sacrificial layer method. The over-coating of the “beadlets” was not consistent since these were not spherical and did not survive heat treatment. Further work is required to optimize the tablet preparation and coating conditions to yield a final product suitable for heat treatment and thermal cycling.

The program achievements and findings are vital to thermal energy storage in a concentrating solar power plant (CSP). It smoothes the cost-to-demand ratios for electricity and affords predictable power generation, especially on days of zero to intermittent sunshine.

Section 6 Path Forward

Even though this project achieved a major breakthrough by making capsules that withstood 5000 thermal cycles using a commonly used manufacturing method with a potential to achieve SunShot cost goal, we recommend further research and development with following activities be conducted:

- Determine the tolerance limits for recipe composition by conducting additional designed experiments around the selected recipe.
- Encapsulate a different salt mixture such as a mixture of MgCl2-KCl or a higher melting salt (prills should be readily available)
- Make beadlets using tableting approach with the selected chemical components. Tests were terminated for lack of time in the project and to concentrate funds on the successful sacrificial method for making capsules
- Make large batch of capsules (a few Kg) with selected recipe at a coating manufacturer
- Design and build a EPCM test bed in joint partnership with a CSP developer
- Test the sacrificial method to encapsulate salts melting at temperatures $>600^{o}C$ for advanced CSP systems.

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