

EuroSun 2010 – A Practical Phase Change Thermal Energy Storage for Concentrating Solar Power Plants

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Abstract

Thermal energy, collected in concentrating solar collectors such as power tower or parabolic trough, can be stored cost effectively and efficiently in phase change materials (PCM) such as inorganic salt mixtures. Storing heat as latent heat in PCM, compared with the more conventional sensible heat method, reduces the amount of molten salt used by 30% and the container size by 60%. However, a major issue that is preventing the commercial use of PCM for thermal storage is that it is expensive to discharge the latent heat stored in the PCM melt. The reason being that when salt solidifies around heat transfer tubes, heat transfer coefficient decreases significantly and requires expensive heat exchangers. Terrafore's innovative approach uses a coated shell and tube heat exchanger and a specific composition of the salt mixtures called a *dilute eutectic*. The combination of using a *dilute eutectic* composition of salt mixture with anti-stick coatings on heat exchanger tubes, and mixing a nucleating agent to the salt mixture allows the salt to freeze as a slurry which can be pumped to an external heat exchanger thereby increasing heat transfer coefficient by forced convection. This paper presents the preliminary results of the on-going research at Terrafore funded by the United States Department of Energy and discusses the benefits of using PCM-TES in solar plants.

1. Introduction

A key technological issue facing the success of future Concentrating Solar Power (CSP) plants is creating an economical Thermal Energy Storage (TES) system. Current TES systems use either sensible heat in fluids such as oil or molten salts, or use thermal stratification in a dual-media consisting of a solid and a heat-transfer fluid.

In a sensible heat storage system, heat is stored as difference in thermal energy between hot and cold fluids [1]. These systems require large volumes of heat storage medium with large tanks which makes the storage costly. On the other hand, TES systems, which use phase change materials (PCMs) in salt mixtures, store heat as latent heat of fusion at a constant temperature. The latent heat of fusion is significantly higher than the specific heat capacity in sensible heat storage systems. The former method reduces the amount of molten salt and the size of the container, thus reducing the cost and heat loss that occurs during storage. Additionally, since heat is stored at a higher average temperature than sensible heat, the thermodynamic conversion efficiency in these systems is higher than the sensible heat storage systems.

However, a major issue that is preventing the commercial use of PCM-based TES is that it is difficult to discharge the latent heat stored in the PCM melt. The reason being that when heat is extracted, the melt solidifies onto the heat exchanger surface and decreases the heat transfer. Even a few millimeters of thickness of solid material on heat transfer surface results in a large drop in heat transfer due to the low thermal conductivity of the solid PCM. Thus, to maintain a desired heat rate, the heat exchange area must be large which increases cost.

A second issue with CSPs is the challenge of finding low cost salt mixtures with good thermal properties and high heat of fusion.

2. Innovative Technology for PCM Thermal Energy Storage (PCM-TES)

2.1 Approach to Improving Heat Transfer in PCM-TES

Terrafore's innovative approach to significantly improving the heat transfer during discharge of heat from PCM salt is to use:

- specific compositions called the *dilute eutectic* of inorganic salt mixtures that have a simple phase diagram. A property of dilute eutectic is that when it freezes, it has an equilibrium liquid associated with it. With a simple phase diagram, there are no solid solutions with the major component. The freezing solid with the associated liquid has the consistency of a slurry and can be pumped to an external heat exchanger. The forced convection heat transfer due to flow velocity in a slurry is significantly larger than the conduction through solid. An example of a dilute eutectic salt mixture would be 96% sodium nitrate (NaNO₃) and 4% sodium hydroxide (NaOH). The mixture is a hyper eutectic in NaNO₃ in that it contains significantly more NaNO₃ than that required to form the eutectic with NaOH. This system forms a simple phase diagram in that there are no solid solutions with the composition other than the eutectic composition and thus, presents a large liquidus region between the selected composition and eutectic composition.
- a 'salt-phobic' coating on the heat exchanger surface to prevent sticking or to reduce the adhesion of the salt to the tubes. In addition, a nucleating agent and chemical is added to the salt mixture to encourage nucleation away from the heat transfer tubes.

2.2 Requirements of PCM-TES for Concentrating Solar Plant (CSP)

Two key considerations for designing a successful PCM storage system for CSP include:

- Selecting a storage media in the approximate melting temperature range of 280 C to 350 C with the following properties :
 - High energy density. This requires less TES material and hence smaller tanks, lower cost, and lower thermal loss during storage.
 - High chemical and thermal cycling stability to 550 C
 - Complete reversibility for a large number of charge and discharge cycles
 - Low specific cost
 - Readily available and easy to handle with low toxicity and corrosivity
- Designing a heat exchange mechanism that minimizes the cost of the heat exchanger. To discharge heat from a PCM-based TES, a good heat exchanger should have the following properties:
 - High heat transfer coefficient throughout the discharge
 - Use low parasitic power or pumping, if using an active heat exchanger
 - Use common heat exchanger designs, such as shell and tube

2.3. Baseline PCM-TES Configuration

The Phase Change Material (PCM) Thermal Energy Storage (TES), design using a single tank is shown in Figure 1.

Figure 1 shows a PCM-based TES system with a single tank in a power-tower configuration. In this configuration, thermal energy is stored in an inorganic molten salt mixture. In the figure, the fluid at the bottom of the tank labeled- PCM Melt- stores about 75% of the total heat at a constant

melt temperature, as heat of fusion in an inorganic salt mixture. The fluid labeled – Hot Molten Salt – stores the remainder 25% of heat as sensible heat in salt temperatures between the melt temperature and up to 540 C. (The melt temperature depends on the selected salt mixture.) Starting from the right of the tank in Figure 1, feed water from the condenser is vaporized into a saturated steam in a steam generator heat exchanger / drum boiler labeled HX-1. Superheat is added to the saturated steam in the super heater heat exchanger labeled HX-2 before the superheated steam is delivered to the Steam Turbine Generator. The heat for superheating steam and vaporizing feed water is provided by pumping the hot molten salt from top of tank, first to HX-2 and then to HX-1 as shown in the figure. The partially-frozen salt-slurry from HX-1 is returned to the tank.

On the left of the tank in Figure 1, the hot receiver fluid from the Solar Central Receiver transfers heat to the molten salt in the tank in a heat exchanger labeled HX-3; then the fluid is directed to the heat exchangers labeled HX-4 to melt the salt in the tank. The cold receiver fluid from HX-4 is returned to the Solar Central Receiver to collect solar heat.

The hot receiver fluid can be any advanced heat transfer fluid such as a thermally-stable molten salt mixture or liquid sodium. Since the receiver fluid is independent of TES fluid, large volume of this fluid is not required. In addition, the hot receiver fluid temperature, shown in Figure 1, at 550 °C, can be raised to be near the thermal constraint of the selected receiver fluid. For example, if this temperature can be increased to 600 °C, then the hot molten salt temperature in the tank can be raised to 580 °C instead of the 540 °C.

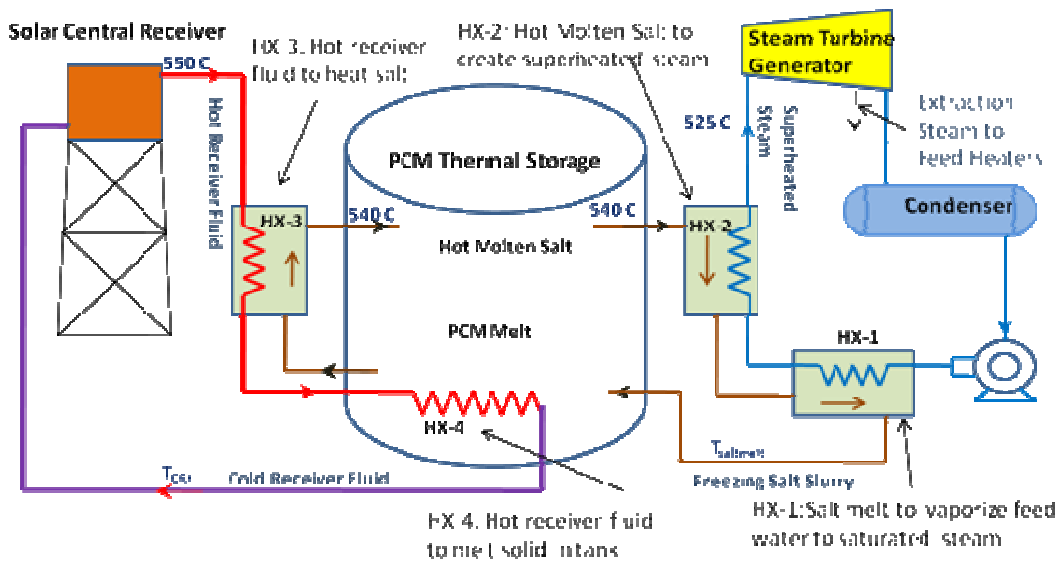


Fig. 1. PCM-based TES design offers a low cost approach by reducing the system size by 37%

There are other possible ways to configure TES systems for any CSP system. For example, we can use two separate tanks—one for hot molten salt and the other for the PCM melt. This reduces the complexity of tank design because there is no large temperature gradient from top to bottom of the tank. However, this design may be costly because of a need for the additional tank. Yet another configuration could use a cascaded PCM [1]. In this configuration, two different PCMs melting at different temperatures are used; one provides the heat to vaporize the feed water and the other provides the superheat.

2.4. Modes of Operation

The CSP-TES system operates in the following modes:

- **Charge Cycle.** In this mode the hot heat transfer fluid from the solar receiver is used to charge or transfer collected heat to the TES tank. During periods of low solar insolation (such as early morning hours) or hazy days, the receiver fluid can be allowed to be lower than the maximum design temperature. In this case, the receiver fluid bypasses heat exchanger HX-3 (bypass not shown in figure) and is used to melt the salt in HX-4. This is an additional advantage of using PCM systems as it can increase the overall collection efficiency.
- **Discharge Cycle.** In this mode the heat stored in the TES tank is transferred to boil high pressure water and superheat it to turbine inlet conditions to generate electric power.
- **Charge while Discharge and vice-versa.** During day the charge cycle mode and discharge cycle can both be active. Heat is added to storage from receiver fluid and heat is discharged from TES to generate steam. In this mode, the hot PCM fluid from HX-3 bypasses the tank directly to the steam generator HX-2 and HX-1 (bypass not shown in Figure 1).
- **Hold Mode.** In this mode there is no active charge or discharge of heat. A small amount of heat is withdrawn from the storage using a smaller pump to heat the pipes from freezing and to generate low pressure steam to keep the turbine on hot standby.
- **Shutdown Mode.** In this mode the TES system is shut down with all pumps turned off and valves at the fail-safe position to perform any system diagnostics or maintenance.

3. Shell and Coated Tube Heat Exchanger Design

3.1. Heat Exchanger Design

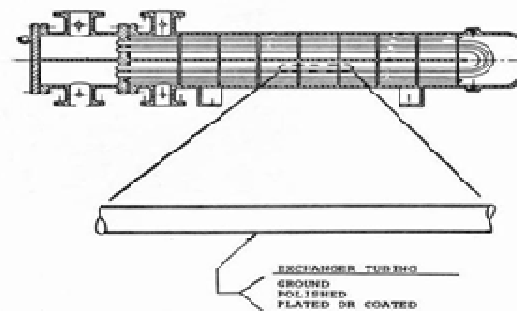


Fig. 2. Shell & Coated Tube Heat Exchanger

There are many types of heat exchangers used in the industry for transferring heat during phase change from liquid to solid. Some of the active (not passive) heat exchange designs described in literature [2] include shell and coated tubes, mechanical scrapers, ultrasonic vibrations, direct contact method, or flexing to free the tubes of freezing salts. Of these the following three methods show promise and are being investigated:

- Using coated heat exchanger tubes
- Encapsulating salt in a suitable shell material
- Providing direct contact of salt with heat transfer medium

Our analysis indicates that the shell and tube type of heat exchangers, with the salt on the shell side and the two-phase steam water inside the tube (Figure 2), is practical and can potentially be economical to use since this is a commonly used design in the industry.

3.2. Salt-phobic Coatings

We surveyed the coatings available and chose those that could handle 500 °C or greater temperatures. Once we had a collection of such coatings, we further selected from this group, coatings that had desirable surface properties such as low roughness and a hydrophobic nature. A hydrophobic surface is considered desirable because it has a low surface energy. What this means is that intermolecular attraction between the surface and a crystallite is limited and as a result, “stickiness” of the crystallite is minimized.

A smooth surface is also highly advantageous for two reasons. Firstly, lock and key binding of the crystallite to the surface is minimized and secondly, the reduced contact surface area minimizes the effect of the intermolecular forces. In effect, the smooth surface enhances its inherent hydrophobic nature.

To this end, we investigated coating materials such as graphite, metallic nitrides and carbides and selected 13 coatings. From this list we then coated the selected samples and tested by dipping them into molten salt and manually studied the salt adhesion.

3.3. Screening of Coatings using Differential Scanning Calorimetry with Coated Boats

In order to screen prospective coatings, small-scale experiments must be performed to test the performance and survivability of the coatings before larger more expensive prototypes can be produced. Thirteen different coatings were identified and selected by observing the adhesion to coated surface when a sample is dipped in molten salt. To further quantify this, differential scanning calorimetry (DSC) is chosen as a technique for its flexibility, small sample size, and accuracy.

A DSC is an instrument which measures heat input versus temperature rise in a material. A sample is encapsulated in a container and placed in a furnace, along with an empty reference container. The temperature of the sample can be controlled very accurately, and the difference in temperature between the reference and the sample allows for calculating heat input into the sample versus temperature. This method allows for measuring many properties such as heat of fusion, specific heat, glass transition temperatures and so on.

The salt samples are processed in the DSC within sealed stainless steel sample pans. The surface finish and coating can be controlled and tested quickly with a variety of different salt mixtures. The effectiveness of the coating can then be measured by the temperature at which the solidification event is observed. If the coating is working effectively, a shift should be observed over an uncoated sample. The DSC also allows for life-cycle testing to determine if the coating remains effective through many freeze-thaw cycles.

4. Heat Transfer Model

4.1. HX-1 Heat Transfer Model

Based on a first principles mathematical model, we can derive the following expression for salt side heat transfer coefficient.

$$h = \sqrt{\frac{k * H_f * m}{V h_x * \Delta T}} \quad (1)$$

Where,

k = Thermal conductivity of salt

ρ = Density of salt

Hf = Heat of fusion

m = Mass flow rate of salt

V_{hx} = Shell side volume of heat exchanger

ΔT = Temperature difference between salt and tube surface

The heat transfer coefficient is a function of the salt properties and operating parameters. Salts with high density, high heat of fusion and high thermal conductivity have higher heat transfer coefficient for a given heat exchanger design. The coefficient decreases with increasing residence time (ratio of shell side volume to volume flow rate) in the heat exchanger. Also, note that the heat rate increases as square root of heat transfer difference in temperature between the salt and surface. Thus, it can be seen that salts with high heat of fusion not only reduce the total salt required but also reduce the total heat transfer surface required.

The increase residence time and increased temperature difference result in higher salt deposition on the tubes and hence lowers the coefficient. For a given heat transfer rate, the higher heat of fusion results in a smaller thickness of salt on tube and hence higher heat transfer coefficient. The increase in coefficient due to higher thermal conductivity is obvious.

Based on this model, we expect the heat transfer coefficient in HX-1 to be greater than 200 W/m²-K, which is significantly higher than the passive heat transfer. The heat transfer area is 25 to 50 times less than that required with passive design. However, there is an additional cost of coating the heat exchanger and operating costs for pumping the salt over the heat exchanger.

4.2. HX4 Heat Transfer Model

Heat is transferred by free convection to the salt from the hot receiver fluid in HX-4. The salt side free convection heat transfer coefficient is a function of the Grashof number.

$$Nu = C (Gr * Pr)^{0.25} \quad \text{for } Gr < 10^7 \quad (2)$$

$$Gr = (D_0^3 * \beta^2 * g * \Delta T) / \nu^2 \quad (3)$$

where

β = Thermal expansion coefficient,

ν = Kinematic viscosity

ΔT = Temperature difference between tube surface and salt and

D_0 = Pipe diameter

Substituting for NaNO₃ properties, we arrive at

$$h = 17.8 (\Delta T/D_0)^{0.25} \quad (4)$$

h (in Btu/hr-ft²-F), ΔT in degree F and D_0 in ft

For nominal conditions, the external heat transfer coefficient for charging is calculated at about 500 W/m²-K or (~90 Btu/hr-ft²-F). Thus once a small amount of melt (~ 1 to 2 cm) is formed around the tubes, convection cells are setup and the heat transfer from HX-4 is by free convection.

A controller is designed to pump flow out from a specified stage in the tank when the melt is formed and when the HTF fluid is higher than the set point temperature of the top of the tank (540 °C). The TES PCM salt picks up the heat from the receiver fluid in HX-3 and flow is controlled to maintain the exit from HX-3 at 540 °C, the set point for the top stratified layer. The remainder heat from the HTF is absorbed in HX-4 for melting the salt.

5. Experiment Design to Test Coated Tube Concept

5.1 Single Tube Tests

A two tank flow loop was developed to recreate the flow and heat transfer conditions in a controlled setting.

Fig. 3 shows a line diagram of the system. The test section consists of a 0.5 inch OD tube with external cross flow through a 5"x5" square cross section. This is intended to recreate the flow

conditions inside a shell and tube heat exchanger. The system is capable of pumping upto 0.02 m³/s (~250 gpm) of molten salt, giving a mean velocity range of 1 meter per second. This allows us to test a variety of heat exchanger flow conditions. The tube is cooled internally using compressed air by a double bayonet heat exchanger. The inlet and outlet temperature, pressure, and flow rate are monitored to determine the amount of heat extracted from the system. Both coated tubes and uncoated tubes will be tested, and the coatings will be evaluated for improved performance.

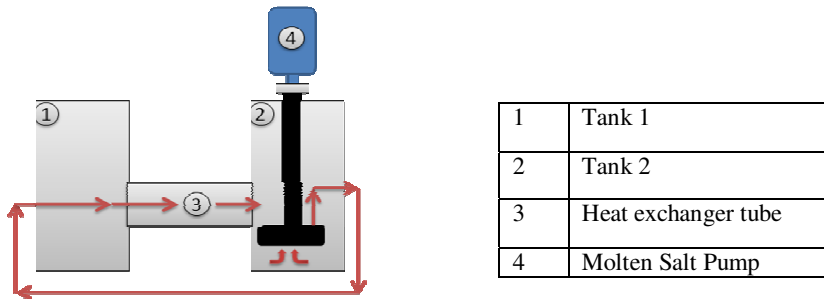


Fig. 3. Line Diagram of Apparatus

5.2 Flow Rig with Coated Tube Heat Exchanger

Once results have been verified in a single tube system, a larger flow rig will be implemented using a more complex heat exchanger. The system will use a flexible mounting system to allow for various heat exchanger arrangements for future testing. The initial experiments will use eighty coated heat exchanger tubes which will allow for a much more direct comparison to a full industrial heat exchanger than the single tube experiments. This flow rig will be capable of upto 0.03 m³/s (~350 gpm) of flow, with velocities depending on the heat exchanger tested. The system will be cooled by high temperature oil.

6. Results

6.1 Salt Selection for CSP

There are numerous salts and salt mixtures that have melting points within the range of the CSP application. Thirty one salt mixtures containing the chlorides, nitrates and hydroxides of sodium and potassium made the screening based on the melting point required for CSP storage and the desired properties mentioned earlier. Of these, only eighteen had the desired simple phase diagram. The recommended salts are listed in Table 1.

Table 1. Selected Salt for Typical CSP Thermal Storage

Major Component (Initial Melting Point)	Minor Component	Steam Pressure for CSP / Rankine cycle
NaNO ₃ -NaCl eutectic (294 C)	NaOH	5.9 MPa
NaNO ₃ (310 C)	NaOH	8.8 MPa
NaOH (318 C)	NaNO ₃	10 MPa
KNO ₃ (337 C)	KOH	12.4 MPa
KOH (360 C)	KNO ₃	16.5 MPa

6.2 Preliminary Differential Scanning Calorimetry Results

Preliminary experiments were conducted to analyze the compatibility of the salt with stainless steel. Figure 4 shows DSC results of a salt mixture in a stainless steel pan.

The three different curves represent three different cooling rates (10, 50 and 100 °C/min). As the cooling rate decreases, a shift in the onset temperature for solidification is observed. The temperature at which the salts effectively solidify is an important parameter for latent heat storage. This effective temperature should be affected by cooling rates, surface morphology and surface composition (chemistry). As surface treatments are applied to the pan a larger shift in this solidification event onset point should be observed. This shift is representative of the effectiveness of the surface treatments that we will employ in extracting latent heat. As coatings are tested, the shifts should be small at slower cooling rates and large at high cooling rates. By observing how the solidification onset temperature is changed by the surface, coatings can be screened at small scale before being subjected to larger scale tests.

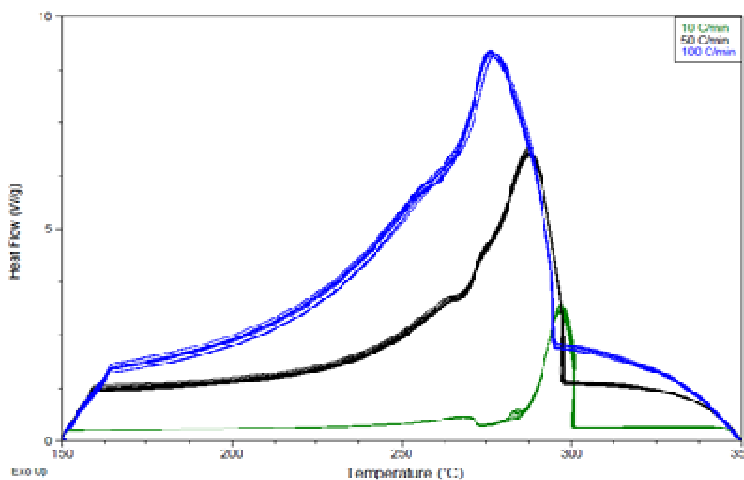


Fig 4. Effect of freezing rate with electropolished boats and nitrate mixture.

7. Conclusion

The active heat exchanger using a shell and coated tube heat exchanger being developed to be used with a phase change thermal energy storage (PCM-TES) for concentrating solar power plants, will significantly improve the heat transfer effectiveness. Using PCM-TES will reduce the size of the thermal storage by over 50% and reduce the cost of the stored thermal energy by over 30% when compared to the conventional sensible heat storage system resulting in reducing the levelized cost of electricity by >5% to 9%. Preliminary results with the coatings and the unique salt mixture composition indicate we will achieve improved heat transfer coefficient.

8. Acknowledgements

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