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Using encapsulated phase change salts for concentrated solar power plant

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Abstract

Storing thermal energy as latent heat of fusion in phase change material (PCM), such as inorganic salt mixtures, can improve the energy density by as much as 50% while reducing the cost by over 40%. However, to discharge stored energy from PCMs, which has low thermal conductivity, requires a large heat transfer area which drives up the cost. Fortunately, salts encapsulated into small capsules can provide high specific surface area thus alleviating this problem. However, a technical barrier with encapsulating salts is that when it is produced, a void must be created inside the shell to allow for expansion of salt when it is heated above its melting point to 550°C. Terrafore's method to economically create this void consists of using a sacrificial polymer which is coated as the middle layer between the salt prill and the shell material. The polymer is selected such that it decomposes much below the melting point of salt to gas leaving a void in the capsule. Salts with different melting points are encapsulated using the same recipe and contained in a packed bed consisting of salts with progressively higher melting points from bottom to top of the tank. This container serves as a cascaded energy storage medium to store heat transferred from the sensible heat energy collected in solar collectors. Mathematical models indicate that over 90% of salt in the capsules undergo phase change improving energy density by over 50% from a sensible-only thermal storage. Another advantage of this method is that it requires only a single tank as opposed to the two-tanks used in a sensible heat storage, thereby reducing the cost from a nominal $27 per kWht to $16 per kWht and coming close to the SunShot goal for thermal storage of $15 per kWht.

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Keywords: Molten salt, encapsulation, phase change material, cascaded thermal storage, concentrated solar power, capsules

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1. 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 over $30 per kWht [1],[2].To economically produce electricity from CSP, SunShot set the goal at $15 per kWht 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 can increase the energy density for storage by as much as 50% and can reduce the cost by over 40%.. However, a major issue that has prevented the commercial use of PCM-TES for CSP is that it is difficult to discharge the latent heat stored in the PCM melt at specified heat rates. This is because when heat is extracted, the PCM-melt which has low thermal conductivity solidifies onto the heat exchanger surface decreasing the heat transfer, and requiring large heat transfer area and hence a higher cost. Thus, to obtain consistently high heat rates, either heat transfer area and /or heat transfer coefficient must be increased. Several methods were unsuccessfully investigated to improve heat transfer coefficient [3].

Encapsulating PCM material inside small capsules increases the specific surface area and using heat transfer fluid in direct contact with the capsules, increases the heat transfer coefficient. However, a technical barrier with encapsulating salts is that a void must be created inside the shell when it is produced. This void is necessary to accommodate the volume increase when melting and heating occur. Under contract with Department of Energy, Terrafore Inc., is researching innovative methods to economically create this void and encapsulate the salt in shell material that can withstand high temperature thermal cycles and will last for more than thirty-year life of a solar plant.

The project's objective is to produce 5mm to 15 mm size capsules containing inorganic salt mixture for storing thermal energy as a combination of latent heat from solid to liquid and as 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^{o}C and must be robust to withstand over 10,000 thermal cycles between 300^{o}C and 600^{o}C. The breakage rate, if any, must be less than 0.1% per year.

Phase-1of the project completed in January 2012, successfully developed a recipe to encapsulate a nitrate salt melting at 370^{o}C in 5mm capsules in a suitable shell material that withstood temperatures to 500^{o}C. Phase 2, currently in progress, is optimizing this recipe and will demonstrate that the capsules can withstand over 10,000 thermal cycles between 300^{o}C and 550^{o}C. Designed experiments and statistical analyses are used to estimate the breakage rate, which must be <0.1% per year and the cost to manufacture these capsules must be less than $5 per kWht. Next step will be to make these capsules on a pilot scale, preferably at a commercial facility, and demonstrate the encapsulated PCM-TES concept on a small scale TES system.

2. Technical details

2.1. Sacrificial polymer encapsulation method and results

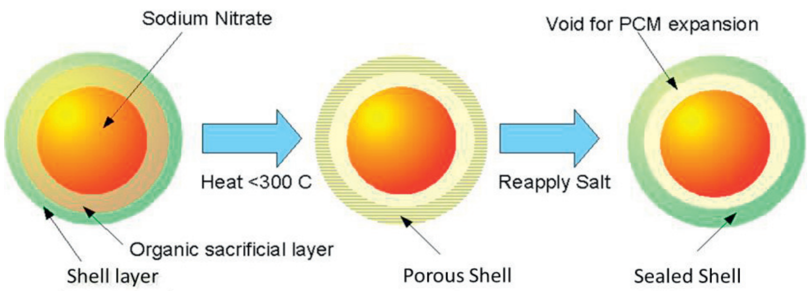

Figure 1 A polymer layer between shell and prill is decomposed to gas to create a void in the capsule

Figure 1 shows a schematic of the 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 on the prill. The capsule thus produced is then slowly heated in a furnace to decompose the polymer and organic binder to gas which escape through the pores of the shell leaving a void around the salt in the capsule. The fluid bed coating 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. The major factors involved in selecting the best formulation and recipe to produce robust capsules are:

- Type and composition of binder, polymer
- Type and thickness of shell coating
- Recipe to decompose polymer by heating

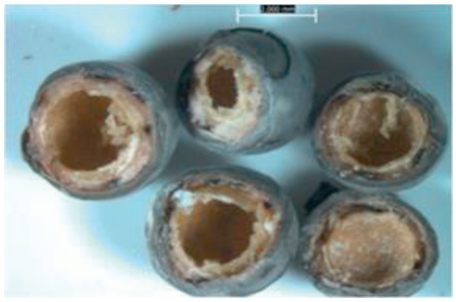

Figure 2 Capsules cut open shows void space to accommodate expansion of salt

Experiments were conducted with different formulations of binders and various film formers including zein, hydroxyl-propyl-methyl-cellulose (HPMC), ethyl-cellulose (Ethocel), hydroxyl-propyl cellulose (HPC), carboxy-ethyl-cellulose (CMC), and poly-vinyl-chloride (PVC). Inorganic fillers tested included carbon black, organically functionalized clay (Cloisite 30B), natural montmorillonite clay (Cloisite NA+), silica, and micronized stainless steel. Solvents for these coating solutions include water, alcohol, acetone, and tetra-hydro-furan. In all experiments, the salt beads used are potassium nitrate prills (NPP-R from SQM). More than 100 experiments with different recipes were conducted using combinations of formulations with varying shell thicknesses and, polymer amounts (for the sacrificial material) to arrive at a successful recipe† for making these capsules. Design of experiment procedure was used to prepare these formulations.

Figure 2 shows capsules which were cut in half after the salt melted and was recrystallized. As shown, the solid salt freezes on the shell and micrographs of the shell show that the shell is porous which is required for the gas to escape.

To test the thermal cycling of the microcapsules, they were cycled ten times between 250ºC and 400ºC to melt and freeze the salt within the capsule. The results are shown in Figure 3, with the differential scanning calorimeter (DSC) curve in green and the TGA in curve in blue. The percent weight loss (blue curve) is relatively stable over the 10 hour course of the run. The DSC results (green) show the melting and freezing, demonstrating the formulation has potential for use in thermal energy storage.

However, to be used in a CSP thermal storage, the capsules must survive over 10,000 thermal cycles which is typical for a 30-year lifetime. Hence, an automated thermal-cycle tester was specially designed and developed and tests are currently underway to test the capsules for this duration. So far, the capsules survived over 2500 thermal cycles in the tester.

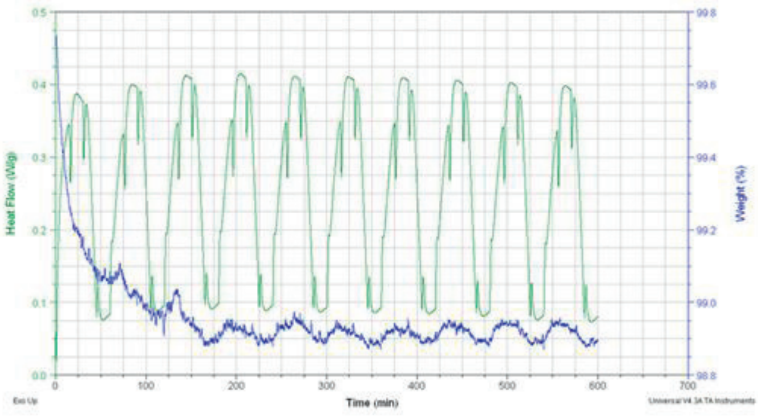

Figure 3 Results of a Capsule Thermal Cycled in a Differential Calorimeter

† Patent Pending

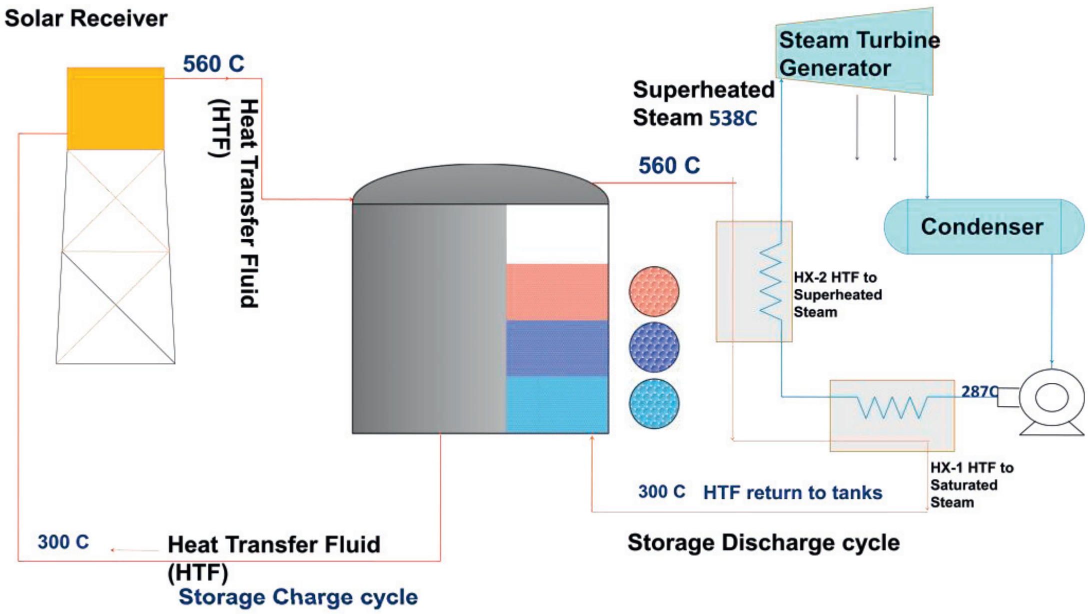

Figure 4 Cascaded encapsulated phase change storage tank with tower solar receiver and Rankine steam turbine power generator shows heat transfer fluid flow during storage charge and discharge cycles

2.2. Cascaded packed bed thermal energy storage

Figure 4 shows a thermal energy storage tank using a packed bed of PCM capsules in a molten salt heat transfer fluid (HTF) such as a low melting molten salt mixture. Figure shows three different PCM salt capsules stacked in the tank. HTF fills the space between the capsules. This cascading is necessary for efficient use of latent heat in PCM as discussed later.

During the storage charge cycle, the HTF which collects heat from the solar collector-receiver (a tower receiver is shown in the figure) is pumped through the packed bed of capsules in the storage tank transferring the collected heat by direct contact with the capsules, first melting the salt and then heating the salt in the capsules to the high operating temperature of HTF as it flows through the bed and exits the tank to be returned to the solar collector. The tank is considered charged when the exit temperature increases by about 5% of the difference between the operating temperatures (eg by 15C or 315^{o}C in the example).

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-preheaterHX-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 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 salt which freezes inside the capsules. The tank is considered discharged when the exit temperature decreases by about 5% of the difference between the operating temperatures (eg by 15C or 545^{o}C in the example).

Thus, heat is stored inside the capsules as sensible and latent heat in the PCM salt in addition to the sensible heat in the HTF contained in the space in the tank that is not occupied by the capsules. The tank is thermally stratified with hot HTF fluid at the top and cold fluid at the bottom of the tank. Because of latent heat, the specific heat capacitance of the capsules is high and therefore a good thermal stratification is maintained.

Since solar heat collected is sensible heat, cascading is required to increase the latent heat utilization of salt inside the capsules and to maintain the temperature of the fluid discharged from the tank. Cascading is achieved by using progressively higher melting point salts inside the capsules. The capsules containing the lowest melting salt are at the bottom and capsules containing the highest melting point salt are at the top. In figure 4, three different types of salt capsules are shown. The melting point of the salt inside capsules at the top of the tank is selected such that it 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 low operating temperature of the HTF. Results, using the mathematical model which is described later, indicate that the melting point of salt in the capsules at the top and at the bottom of the tank should be the desired cut-off point temperatures. The cut-off point temperatures are the temperatures at end of charge and discharge cycle. For example, since a thermocline is established in the tank, the HTF temperature delivered to steam generator HX-2 during discharge cycle remains constant at the high operating temperature throughout the discharge period and typically begin to decrease when about 95% of energy stored is depleted. This cut-off temperature is typically 15C from the design operating temperatures of 560^{o}C and 300^{o}C shown in figure 4. Thus the desired highest melting point of the salt is about 545^{o}C and the lowest melting point of salt at bottom of tank is about 315^{o}C. Other factors such as availability and cost should be considered in addition to the melting point. The capsules in the middle of the tank can contain a salt that melts between the operating temperatures. Analysis using mathematical model indicates there is significant freedom in selecting the bed material(s) for the middle layer(s). Also, the height of the capsule beds can be optimized using the model and cost of salts.

2.3. Results of the mathematical model

A mathematical model was developed to analyze the dynamic behavior of an EPCM thermal energy storage system using spherical capsules filled with phase-change-material (PCM) which were subjected to repeated charging and discharging processes [6],[7],[8].The model solves the energy equation to obtain the transient axial variation of temperature in the heat transfer fluid (HTF) and the radial variation of temperature in the spherical capsules at any axial location while the melting/solidification of PCM within the spherical capsules are modeled using the fixed grid enthalpy-porosity approach. The mathematical model was used to study various design parameters for designing the cascaded encapsulated-phase-change-material (EPCM) TES. Some of the design parameters included – capsule size, the melting point of phase change salt(s), cascading of salt capsules in the tank with progressively higher melting salts, using granite for middle layer, cut-off temperature, and flow velocity. A summary of the results from the analysis [8] is as follows:

- The capsule size is an important design parameter. As capsule size increases, the surface area to transfer heat from capsule to heat transfer fluid decreases. Also, the time to transfer the energy by freezing or melting the salt in the capsule increases resulting in lower utilization of latent heat of all the salt in the tank. In fact the salt inside the capsules at top of the tank does not completely solidify during discharge cycle. Similarly, the salt in the capsules at the bottom of the tank does not completely melt during the charge cycle. Thus, smaller radii capsules yield higher latent utilization of the latent heat in a single tank TES.
- An optimum capsule radius is determined by a trade-offs between capsule size, effective latent energy used. Our analysis indicated that capsule diameter should be between 10 mm to 12 mm for salts with heat of fusion of about 180 kJ/kg. As the heat of fusion of salt increases the optimum capsule size decreases. This is because for a given capsule size as the latent heat of fusion of salt increases, there is more energy to be transferred at a specified heat rate to achieve complete solidification/ melting inside the capsule at top or at the bottom respectively.
- Placing capsules containing salts melting at progressively higher temperatures in the packed bed (with the lowest melting point salt at the bottom), creates a cascaded PCM thermal storage in a single tank. This cascading is required to effectively transfer sensible heat collected in heat transfer fluid and store it as latent heat[4][5]. Using three salts melting at 315^{o}C, 430^{o}C, and 545^{o}C the model indicated that 92% of latent heat in the salts is used for storage when operating temperature is between 300^{o}C and 560^{o}C.
- The effective storage density (latent heat utilized and sensible heat in salt) for a selected capsule size and cut-off temperatures, increases until a Stefan number of 0.5–0.6 beyond which it levels off (Stefan number is the ratio of latent heat of fusion to specific sensible heat energy between operating temperatures).Though

the storage tank size decrease for salts with high latent heat of fusion, the decrease is not proportional to heat of fusion and also smaller capsule radius is required for extracting the latent energy. For example, for a given design, doubling the heat of fusion of salt at the top layer of the tank does not reduce the bed height of salt at the top by 50%. In fact, the top salt layer bed height is reduced by only 15%.

3. Comparing costs of encapsulated packed bed TES and two-tank TES

The cost of the EPCM-TES is compared with a two-tank sensible heat TES using molten salt. Table-1 shows a breakdown of costs and the assumptions to arrive at these two systems. The second column in the table shows the baseline specific cost‡ used in this analysis. These costs are illustrative and the actual costs depend on site, supply and demand of material, and economies of scale. The percentage reduction in TES cost is important for this analysis. The HTF salt and storage media are same for the two-tank TES and assumed to be a nitrate mixture. The cost of the PCM salts in the capsules is assumed to be that for a nitrate salt for the lower melting salt and a carbonate salt mixture for the higher melting salt. The EPCM tank is filled 70% by volume with salt capsules and the remainder with the HTF salt. 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. The specific cost of EPCM TES is 40% lower than the two-tank TES with these assumptions.

4. Conclusions

Phase change salts were successfully encapsulated with a void in the capsule to accommodate for expansion of salt on melting. Initial tests with few thermal cycles in a differential scanning calorimeter indicated the salts melt and freeze in the capsules and stay intact. Tests are underway to demonstrate the capsules can withstand over 10,000 thermal cycles which roughly correspond to a 30-year lifetime.

Using encapsulated phase change materials is perhaps the best method for storing latent and sensible energy because heat rates can be sustained throughout the charge and discharge process while utilizing over 90% of the latent heat of fusion. Optimum capsule diameter is between 10mm to 15mm for salts with nominal heat of fusion of 200 kJ/kg. The optimum size is determined by trading-off pressure drop through the bed and storage effectiveness. Larger capsule size reduces storage effectiveness but reduces pressure drop. To effectively transfer sensible heat collected in solar collectors a three-salt cascaded thermal storage is required with two of the salts having melting points at operating cut-off temperatures and a third salt with melting point between the operating temperatures of solar collector system. For example, for solar operating temperatures of 300^{o}C to 560^{o}C, the recommended salt melting points are 315^{o}C, 430^{o}C, and 545^{o}C. However, the lowest cost and readily available salts at or near these temperatures are economical. Using encapsulated storage reduces the specific costs of the thermal storage closer to the SunShot goal of $15 per kWht. For the example system of 3500 MWht typical of a baseloaded 100 MWe solar plant the specific costs are 40% lower at $16 per kWht compared to a $27 per kWht for a conventional two-tank system..

References

[1] Kelly B., K. D. (July 2006). *Thermal Storage Commercial Plant Design for a 2-Tank Indirect Molten Salt System.* NREL /SR-550-40166.

[2] LUZ Industries, I. (October 19-20, 1988). Thermal Storage for Medium Temperature Solar Electric Power Plants. *Phase-Change Thermal Storage Symposium.* California, USA.

[3] LeFrois. R. , Mathur A. (1982). Active Heat Exchanger Evaluation for Latent Heat Thermal Energy Storage Systems. *ASME*, 82-HT-7.

[4] Gomez J., G. G. (2011). *High Temperature Phase Change Materials for Thermal Energy Storage Applications.* NREL Contract No. DE-AC36-08GO28308.

‡ Obtained by private communication with J. Stekli, Department of Energy..

[5] Michels, H., & R., P.-P. (2007). Cascaded latent heat storage for parabolic trough solar power. *Solar Energy*, 81:829-837.
[6] Beasley, D. C. (1984). Transient response of a packed bed for thermal energy storage. *Int. J. Heat and Mass Transfer*, 27, pp 1659 -1669.
[7] Nithyanandam K.. (May, 2013). *Investigations on Latent Thermal Storage Systems for Concentrating Solar Power.* Blacksburg, Virginia: PhD Dissertation, Virgina Tech.
[8] Nithyanandam K, Pitchumani R., Mathur A., (July 2012). Analysis of a Latent Heat Thermocline Energy Storage for CSP. *Proceedings of ASME 2012 6th International Conference on Sustainability and 10th Fuel Cell Science, ESFuelCell2012.* San Diego, California: ASME.

Table 1. Comparison of Costs for EPCM-TES and Two-Tank TES

		Two-tank TES		***TerraCaps* PCM TES**	
Storage Capacity	MWht	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 / Ht	m	39 / 15.2		32 / 15.2	
Base Area	m2	1195		804	
Surface Area	m2	2225		1891	
Tankage					
Foundations, $/m2	$1,199	$	2,864,628	$	964,293
Platforms & Steel, $/m2	$292	$	697,641	$	234,840
Hot Storage Tank (SS), $/m2	$6,332	$	14,090,301	$	11,973,732
Cold Storage Tank (CS), $/m2	$3,799	$	8,453,736	$	-
Distributors and additional Tank costs	est	$	-	$	1,000,000
Tank Insulation, $/m2	$206	$	1,776,388	$	635,056
Tankage subtotal		*$*	*27,882,694*	*$*	*14,807,922*
Tankage Specific Cost	*$/kWht*	*$*	*7.97*	*$*	*4.23*
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	$	2,040,000
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*	*$*	*13,620,000*
BOP Specific cost	*$/kWht*	*$*	*4.08*	*$*	*4.18*
Storage Media					
Capsule processing (est)	$0.25/kg	- $	-	$	5,384,616
Salt (HTF @$1.25/kg, PCM@$0.75/kg)	$1/kg	$	41,666,666	$	16,153,847
Energy for Salt Melting	est	$	145,000	$	145,000
Media subtotal		*$*	*41,811,666*	*$*	*20,337,308*
Media Specific Cost	*$/kWht*	*$*	*11.95*	*$*	*5.81*
TES Direct Costs Total		$	83,964,361	$	49,765,230

TES Direct Cost Specific	**$/kWht**	**$**	**23.99**	**$**	**14.22**
Engineering - (7% of direct)	*$*	$	5,877,505	$	3.483,566
Sales Tax (8% of direct)	*$*	$	6,717,149	$	3,981,218
TES Installed Cost, Total	$	$	96,559,015	$	57,230,015
TES Installed Cost, Specific	**$/kWht**	**$**	**27.59**	**$**	**16.35**