Conception and Design of a Thermal Energy Storage System

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Abstract: - In order to provide the capability of a thermal storage to produce superheated steam with a temperature of about 330^{o}C (pressure 70 bar), a new phase change material based on a Tin-Zinc alloy was explored as the heat storage medium. It was shown that 70 wt% Zn in the alloy would be optimal to attain a thermal storage temperature of 360-370^{o}C, using solar superheated steam 400^{o}C as the heat charging fluid. At the stage of heat discharge, high quality steam is produced on the base of utilizing mainly the phase change heat of zinc solidification and partly sensible heat of the liquid phase. A heat transfer fluid (e.g. DOWTHERM-A) is used to enhance heat transfer between the storage medium and built-in heat exchangers by the effect of reflux evaporation-condensation. Since the storage process is essentially non-isothermal, a secondary, relatively small thermal buffer following the main storage is required to stabilize the steam outlet temperature. The results of calculations for a pilot of 5MWh thermal storage show that steam sent to a turbine after the buffer may have a temperature near 330^{o}C during the entire charge-discharge cycle comprised of 6 and 1 hr periods respectively.

Key-Words: - thermal storage, zinc alloy, reflux, heat transfer, solar steam

1 Introduction

Concentrated solar power is an environmentally clean and secure source of energy for generation of electricity and production of high-temperature process heat for chemical plants. In order to increase dispatchability of solar power, solar plants need to be accompanied with adequate thermal storage capable of producing energy on-demand, independently of solar collection, a few hours daily.

Utilization of phase change materials (PCM) for thermal storage has the advantage of operating at isothermal conditions with constant power throughput. Systems considered in the literature for various thermal applications are mainly inorganic salts, single and mixtures, which are melted, storing latent heat at the temperature of fusion [1]. However, molten salt systems impose a principal heat transfer problem on the storage design.

The main difficulties encountered with heat transfer in molten salts are those associated with crystalline deposit on heat transfer surfaces that grows continuously and increases the thermal resistance to both heat input and output. In addition there are mechanical issues during the charging step associated with melting of the salt that usually results in an increase of the volume of the liquid.

2 Thermal Storage Solution

This study evaluates a latent heat storage that makes use of new phase change materials in combination with an improved heat transfer concept. The thermal storage is primarily designated to the parabolic trough technology for solar power electricity plants with the process steam temperature around 400^{o}C.

The concept under development is based on combined phase change effects of melting and vaporization in the thermal energy storage medium. A low melting point substance, for instance, liquid metal or synthetic organic oil which is added to PCM, delivers thermal energy from the storage medium to a heat exchanger by the effect of reflux evaporation-condensation. This process of heat transfer is similar to one effectively utilized in heat pipes and pool-boilers. A specific requirement is that the storage vessel must be thoroughly evacuated from water vapors and gases in the beginning and kept continually tight for both vacuum and pressure conditions.

The choice of the heat transfer fluid involves several prerequisites including high-temperature stability; chemical compatibility and minor mutual solubility with the PCM and the structural material; low density in comparison with

PCM; significant vapor pressure at the storage temperature. Feasibility of this concept was demonstrated using a sodium-metal-sodium-chloride system under a storage temperature of 800°C [2].

3 Heat Flow Scheme

Figure 1 illustrates the schematic of Reflux Heat Transfer Storage (RHTS), thermal process that is taking advantage of the increased heat flow rate during evaporation and condensation of a heat transfer fluid (HTF). The function of HTF is to provide efficient heat exchange between the storage and two special heat exchangers (HE) located at the top and the bottom of the PCM compartment. The top HE is fed with high pressure water producing superheated steam during the storage discharge. The bottom HE is used to charge the thermal storage. It is immersed in liquid HTF and connected to a heat carrier (i.e. solar steam).

During heating, the HTF pool is boiling generating an intensive flow of vapors up through the transport channels distributed in PCM. The latent energy of vapor condensation is transferred through the tubes surfaces to PCM. Under discharge, the heat flow direction is reversed, so that HTF evaporation is caused by PCM and the vapors transfer heat to the steam generator via condensation.

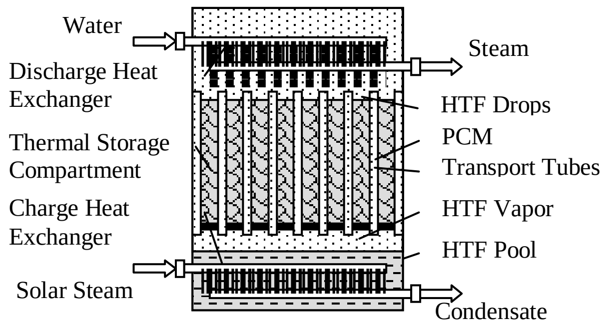

Fig. 1. Layout of the RHTS concept

From a study on selection and characterization of materials, the proper combination of PCM and HTF for RHTS was concluded as follows.

PCM: Tin-Zinc alloy containing 50 to 70 wt% Zn is the storage medium that allows operating at temperatures up to 350 - 370°C, provided the temperature of solar superheated steam supplying heat to the storage is 400°C at the lowest. This material has a high thermal conductivity, roughly 50 W/m-K in liquid state (solids: Sn-63, Zn-112 W/m-K) that is a significant advantage over molten salts and other non-metallic PCM. On discharge, the steam production stage makes use mainly of the phase change heat of zinc solidification and partly of sensible heat of the alloy liquid phase, while the storage temperature drops gradually about 100°C down.

HTF: Commercial high-temperature HTF such as DOWTHERM-A revealed compatibility with the Tin-Zinc alloy at storage temperatures up to 400°C. The reflux HTF flow may produce vapor pressure up to 8-10 bars in the storage system [3]. It is important to free completely the apparatus of incondensable gases in order to avoid blocking of the heat transfer surfaces from a direct contact with the condensed HTF.

4 PCM Calorimetry

Figure 2 shows the Zn-Sn equilibrium phase diagram based on thermodynamic data [4]. It has a eutectic temperature at 198.5°C with a Zn fraction around 9 wt%. Main physical states are: above the liquidus - entirely liquid mixture, below the eutectic temperature – entirely solidified alloy, the middle part is composed of liquid Tin and partly liquid, partly solid Zinc at the same temperature. The effective heat storage region is to the left of the eutectic point and below the liquidus.

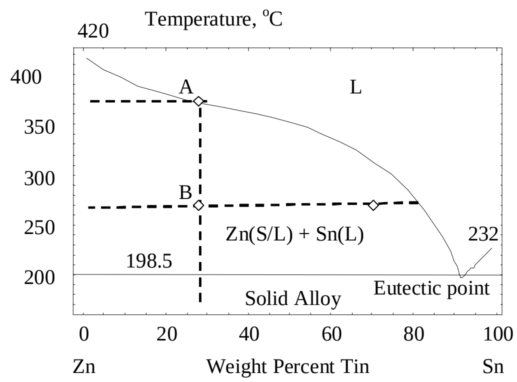

Fig. 2. Zn-Sn phase diagram

Consider point A located on the liquidus curve in Fig. 2 with a composition 30 wt.% Sn + 70 wt.% Zn and a temperature 370°C. As soon as cooling is applied, the mixture starts to produce some solid zinc. While the temperature continually drops, the amount of zinc solidified gradually increases and a composition of the remaining liquid becomes proportionally richer in tin. As a result, the temperature needed to freeze the remaining zinc becomes lower. In so far as the eutectic point, only 3 wt% Zn remains dissolved in the tin, the rest of the Zn is solidified. Upon heating, the system can be reversibly returned back into the initial molten state, above the liquidus. In the calculations performed for the system calorific properties, it was assumed a simple mixture relation, i.e. arithmetic average, using fusion enthalpies (H_{fus}), and specific heat (C_p) coefficients of liquid and solid Zn and Sn from [5].

Under the temperature decrease of 100^{o}C, between points A and B (Fig. 2), the total enthalpy change of PCM is -107 kJ/kg, which composed of the sensible heat of liquid -37 kJ/kg and the released heat of fusion of zinc -70 kJ/kg. Plainly, zinc phase change is a dominating factor in this process, the more zinc in the composition and greater the temperature difference, the higher energy storage capacity is attained.

A PCM composition of 100% zinc could be most favorable for the heat storage, since the heat of fusion of pure zinc is ΔH_f =112 kJ/kg and no temperature difference demanded on charge and discharge. However, the melting point of zinc 420^{o}C is too high for the solar steam process of interest. Presently, the solar superheated steam, as the storage heat carrier, is supposed to have a temperature 400^{o}C (pressure 70 bar). This limits the zinc percentage in Sn-Zn alloy at no more than 70wt% in order to have a sufficient temperature gradient of at least 30^{o}C between the solar steam and the PCM.

Heat of fusion for Zn is rather low as compared to typical salt-based materials, e. g. $NaNO_3$ (melting point 307 ^{o}C, ΔH_f = 172 kJ/kg). Nevertheless, the zinc alloy, metallic PCM may benefit from practically unlimited chemical stability, high substance density, and superior thermal conductivity.

5 Thermal System Layout

Heat storage capacity in the A-B process could be increased if the temperature difference was further extended, mainly on account of a reduced temperature B. Then, the temperature of steam produced on discharge would drop approximately over the same temperature range, equal or larger than 100^{o}C, from the beginning to end of the process. However, steam temperature variations over 10-20^{o}C would reduce significantly the steam turbine efficiency.

In order to narrow the steam temperature range produced by a non-isothermal storage, the following solution is suggested. Depicted in Fig. 3, thermal storage is assembled of two RHTS-based elements: the main energy storage unit, and a thermal buffer, which is set to leveling the time-variable temperature of steam after the main storage. With the same PCM filled in both units, the buffer, as shown farther, is much smaller in size than the main storage. Functioning of a buffer is explained as: a) at the beginning of charge phase the buffer must be at a higher temperature than the main storage to be able to partly compensate the significant drop of steam temperature occurred in the main storage, b) later, during the charge, as the main storage temperature is increased, the steam temperature may gradually become higher than that of the buffer, then part of steam energy is transferred to the buffer, recovering its temperature, and c) the process is overturned on the discharge, working to retain the steam temperature at a given level.

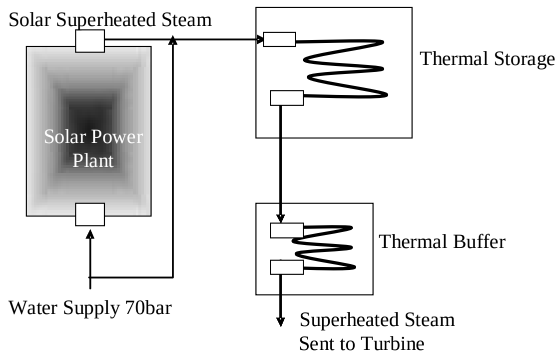

Fig. 3. Two-stage RHTS module integrated in a solar power plant.

The scheme assumes that solar superheated steam produced during sunlight hours, for instance, at a pressure 70bar (water boiling point 287^{o}C) and temperature 400^{o}C can in series charge the thermal storage module and feed the industrial process, i.e. a steam turbine. It means that part of the sensible heat of steam is utilized for thermal storage by heating the PCM closely to a temperature 370^{o}C. Though, after the thermal storage module, the quality of the superheated steam becomes reduced, correspondingly to a temperature 330^{o}C, it yet may be sent to operating the turbine. Out of solar energy supply, partly or absolutely, the thermal storage would be capable of producing superheated steam of the same quality for a period of tens minutes to few hours, depending on the storage size.

5.1 Simulation of a 5MWh RHTS System

Pilot scale storage parameters for a direct steam solar power plant were analyzed by the method of thermal energy balance equations written the same for either main storage or buffer unit. In the set of equations below, Eq. (1) describes the change of PCM enthalpy $\mathbf{E_{PCM}}$ (quantity $\mathbf{m_S}$, bulk temperature $\mathbf{T}$) in time, Eq. (2) - enthalpy change of fluid (water/steam with mass flow rate $\mathbf{M_F}$) between outlet and inlet, including water-steam phase transition, Eq. (3) – heat transfer in each heat exchanger being composed of convective heat transfer coefficient **k**, surface area **A**, and log mean temperature difference between PCM and fluid **ΔT**, and Eq. (4) – overall balance of heat in the system at any time (**t**).

$$q_S = m_S \frac{d\,E_{PCM}[T[t]]}{dt} \qquad (1)$$

$$q_F = M_F\,(E_F[T_2[t]] - E_F[T_1[t]]) \qquad (2)$$

$$q_{HE} = k\,A\,\Delta T[t] \qquad (3)$$

$$q_F = q_S = q_{HE} \qquad (4)$$

Initial conditions comprised a set of the following parameters:
Beginning of charge:

- Storage temperature T_{SC};
- Buffer temperature T_{BC};

End of charge:

- Storage temperature T_{SE};

Beginning of discharge:

- Storage temperature $T_{SD}= T_{SE}$;
- Buffer temperature $T_{BD}= T_{BE}$;

Steam temperatures at the main storage outlet and buffer inlet were assumed equal continuously. No heat losses and pressure drop were considered. In addition, complex calculations of heat transfer coefficients were replaced at this stage with rough estimations relevant to the problem. Table 1 gives the input values used in the pilot storage system calculations.

Table 1. Data applied in the storage simulation.

Water/Solar Steam flow rate	kg/s	8.0
Water temperature	^oC	250
Solar steam temperature	^oC	400
Storage temperature $\mathbf{T_{SC}}$	^oC	300
Storage temperature $\mathbf{T_{SE}}$	^oC	360
Buffer temperature $\mathbf{T_{BC}}$	^oC	340
Storage PCM mass	ton	500
Buffer PCM mass	ton	100
Heat transfer coefficient **k**: Steam-to-PCM, Combined process- Water/Boiler/Steam-to-PCM	kW/m^2K	 0.1 2.0
HE surface area **A**: Storage built-in Buffer built-in	m^2	 1200 300

Values of the product **k*A** were adjusted to obtain a small temperature difference **ΔT** in Eq. (3), about 10^{o}C. Separately the numerical values of **A** make no sense because of a virtual meaning given to the coefficient **k** in present calculations.

Figure 4 shows the calculated temperatures for one full charge-discharge cycle. It follows from the results obtained that a complete charge of the main storage takes 6 hours, with storing 5 MWh thermal energy. This storage capacity allows full throughput of superheated steam during about 1 hour continuously. A series of short discharge periods was considered too. From Fig. 4, the effect of buffering upon steam temperature variations in time can be recognized clearly. Comparing curves 1 (main storage outlet) and 2 (buffer outlet) for the discharged period shows that installing the buffer unit after main storage changed the overall steam temperature difference from about 70^{o}C to maximum 20^{o}C. During the whole operational cycle, steam sent to the turbine has a quite stable temperature 320-340^{o}C.

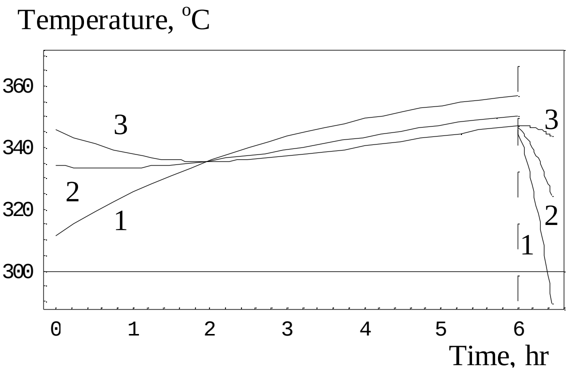

Fig. 4. Temperature variations during one continuous cycle of 6hrs charge and 1hr discharge: 1- Steam exiting main storage, 2- Steam exiting buffer, 3- Buffer PCM.

6 Conclusion

A Reflux Heat Transfer Storage (RHTS) concept based upon integrating of physical processes of storing and transferring thermal energy has been developed for applying it to a solar power steam technology (specifically the parabolic trough). Tin-Zinc alloy and DOWTHERM-A were selected for this study as latent heat storage and reflux heat transfer fluid respectively. The alloy composition was optimized at 30wt% Sn - 70wt% Zn from viewpoints of PCM calorific property, steam temperature and storage capacity. To design the thermal storage module for a 5 MW solar power plant, a numerical simulation using thermal energy balance equations was carried out under the solar superheated steam temperature of 400^{o}C and various other operating conditions.

It was demonstrated that installing a relatively small buffer unit (100 ton PCM) following the main storage (500 ton PCM) for leveling the temperature of steam sent to the turbine allows stabilizing the output temperature at 320-340^{o}C during the entire charge-discharge cycle. With estimated thermal capacity 5 MWh following 6 hours of charging from the solar steam, the period of steam production rated at 8 kg/s is about 1 hour.

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