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# Testing a new design of latent storage

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## Abstract

A modified spiral plate heat exchanger used as latent storage module for direct steam generation was proposed in the REELCOOP project. Under the failure of eight other phase change materials claimed in the literature as potential latent storage media, the phase change material used to meet the temperature range needed is the Hitec<sup>®</sup> salt. This paper presents the melting/ freezing tests performed with the Hitec<sup>®</sup> salt previous to its use in the storage module, the general scheme of the experimental facility constructed at the Plataforma Solar de Almeria, as well as the acquired know-how during the filling of the TES module and the commissioning of the facility.

Keywords: Latent storage, phase change material, Hitec<sup>®</sup> salt.

# 1. Introduction

One of the objectives in Prototype #3 of the REELCOOP project (7<sup>th</sup> Framework program of the European Union Ref N. 608466, www.reelcoop.com) is to drive an organic ranking cycle (ORC) using parabolic trough solar collectors with direct steam generation combined with a biogas boiler. In order to cover the gap between the full operation of the biogas boiler and the absence of solar radiation, a latent thermal energy storage was planned.

At Ciemat-Plataforma Solar de Almería, a modified spiral plate heat exchanger for its use as thermal energy storage (TES) has been selected for its test using Hitec<sup>®</sup> salt as storage medium. This salt has been tested both in nitrogen and argon atmospheres in order to demonstrate the feasibility of this material as phase change material (PCM).

The TES has been installed at the Plataforma Solar de Almería where some issues had to be solved previous to performing the tests. During the commissioning some problems had to be addressed: mainly the filling of the spiral thermal energy storage module and the presence of water remaining from a previous pressure test.

The present paper is organized as follows. The phase change material selected is presented in the next section and the tests performed with Hitec<sup>®</sup> salt are presented; section 3 presents the concept of the storage module. Section 4 describes the facility operation modes, while section 5 outlines the main issues solved during the commissioning. Finally, section 6 summarizes the main conclusions.

## 2. Phase change material selection

The working temperatures of the ORC machine in the REELCOOP Prototype#3 are in the range of 130  $^{\circ}$ C – 170  $^{\circ}$ C, and hence the material storing the thermal energy has to change phase in the same range of temperature.

From the several compounds suggested in the literature (Sharma and Sagara, 2005; Waschull et al., 2009) as good candidates for latent storage, D-mannitol, hydroquinone and salicylic acid were previously tested by Bayón (2015). Hydroquinone and salicylic acid presented a strong vapor emission upon melting, and D-

mannitol displays supercooling during freezing, a decrease of the melting temperature and enthalpy together with a strong degradation under just few freezing/melting cycles. This degradation process of the D-mannitol can also be observed after melting/freezing cycling in both nitrogen and argon atmospheres (Rodríguez-García, 2016). Another four materials were also considered (X165, Galactitol, CaCl<sub>2</sub>·2H<sub>2</sub>O, KNO<sub>3</sub>-Ca(NO<sub>3</sub>)<sub>2</sub> and LiNO<sub>3</sub>-KCl) and all disregarded, either for being available at only specific shapes, or changing phase at a temperature a bit higher –around 190 °C-, or having a thermochemical reaction more than a phase change, or becoming hydrated or for promoting pit corrosion)

The finally selected PCM was the Hitec<sup>®</sup> salt (NaNO<sub>3</sub>-KNO<sub>3</sub>-NaNO<sub>2</sub>; 7/53/40 % w). The freezing point of this salt is 142 °C, presenting stability up to 535 °C. Other properties reported by Serrano-López et al. (2013) and Vignarooban et al. (2015) are stated in Tab. 1. This salt has been selected despite the relatively low enthalpy of fusion because its melting temperature fits in the selected temperature range, and because of its chemical stability when melting/freezing cycled.

Density, p, [kg/m <sup>3</sup> ]	Thermal conductivity	Heat capacity	Enthalpy of fusion	Cost
(T expressed in Kelvin)	λ, [W/mK]	Cp, [J/kgK]	$\Delta H$ , [kJ/kg]	[\$/kg]
ρ=2279.799- 0.7324·T	0.48	1560	83.6	0.93

Tab. 1: Thermal and physical properties of Hitec® salt.

Sohar, M.S. et al. (2013) describes that  $Hitec^{\$}$  salt is somewhat hygroscopic, containing absorbed moisture. Nitrite salt present in the  $Hitec^{\$}$  mixture can change to nitrate in O<sub>2</sub> presence, as shown in eq.1, increasing the fusion temperature of the mixture.

$$2NaNO_2 + O_2 \rightarrow 2NaNO_3 \qquad (eq. 1)$$

At the same time, the presence of water sustains the electrochemical corrosion mechanisms usually associated with aqueous systems, including galvanic corrosion. In order to avoid this, nitrogen has to be circulated through the TES module in the Hitec<sup>®</sup> channel.

The thermal behavior of Hitec<sup>®</sup> as phase change material, and its degradation after 50 melting/freezing cycling between 120 °C and 165 °C under inert atmosphere has been tested. Although nitrogen is cheaper than argon, it could somehow react with the molten salt, changing its chemical composition. According to this, both argon and nitrogen atmospheres have been considered for the tests.

The testing device is the one described by Rodríguez-García, M.M. et al. (2016). The melting/freezing cycles reproduce the "standard" daily operation conditions in a commercial plant. Understanding "standard" as a sunny day where the salt is melted sometime during the day (charging process), storing the energy for some hours and then giving up its latent energy to the water, i.e. the salt freezes, at a certain point of the day, e.g., the sunset (discharging process). In the tests, the salt is melted, keeping it liquid for 12 hours. After this period the salt provides its latent energy while it freezes, remaining frozen until the 24 hours are completed and a new cycle starts.

The fig. 2 (left) displays temperature/time curves of a 20 g Hitec<sup>®</sup> sample for the 1<sup>st</sup> and the 50<sup>th</sup> melting/freezing cycles under N<sub>2</sub> atmosphere. As can be seen the melting temperature interval for the first cycle has a well-defined plateau at 142 °C – 144 °C corresponding to the Hitec<sup>®</sup> salt melting that lasts around 10 minutes. The curve corresponding to the 50 cycles overlaps with the first cycle curve, and the melting temperature interval fits very well to the first cycle. The same can be said for the melting/freezing cycles under Ar atmosphere, as can be seen fig. 2 (right). As a result of these tests we can say that no degradation after melting/freezing cycling has been observed.



Fig. 1: Melting/freezing cycles of Hitec<sup>®</sup> in N<sub>2</sub> (left) and Ar (right) atmosphere.

## 3. Storage module

The proposed thermal energy storage design concept has a double spiral plate geometry, where one of the channels is filled up with the phase change material, remaining still along the time. Through the other channel runs the water in vapor or liquid state depending on the operation mode (charge of discharge). As stated by Rivas et al. (2012), this geometry presents a large energy exchange surface by unit volume providing an effective heat transfer, in spite of using storage medium with low thermal conductivity as most inorganic PCM have and that follows solid to liquid transitions to store the energy.

Patented by Rivas et al. (2011), the module tested in the REELCOOP project is an adaptation of a commercial spiral plate heat exchanger, due to limitations in budget and project time frame.

With 825 mm diameter and 1000 mm height, the spiral heat exchanger used as TES module has volume at the water/steam channel of 205 liters, and 230 liters at the molten salt channel. The effective heat transfer area is 29.3 m<sup>2</sup>. The expected thermal capacity is 6 kWh, assuming a latent enthalpy of 50 kJ/kg, which is the figure we have obtained in the DSC tests we have previously performed (in previous literature a figure of around 84 kJ/kg can be found).

The TES module has been provided with thermocouples to follow the temperature evolution during the charging and discharging processes. Thermocouples were inserted through the four connecting flanges as represented in fig. 2a. Due to the internal structure of the TES module, with double spiral plates separated by separators, no additional thermocouples could be inserted at intermediate plates. Nitrogen injection lines were installed at the connecting flanges of the PCM channel (B1 and B2 in fig. 2a).

Once the instrumentation was settled at the TES module, this latter was installed adapting an already existing thermal storage testing facility, initially connected to the PSA Direct Steam Generation facility (DISS) but that was adapted, becoming independent of such a solar dependent facility. See Fig. 2b.



Fig. 2: a.- TES Temperature sensors and  $N_2$  line. b.- Installation of the TES module at the PSA facilities.

#### 4. Facility operation description

The used testing facility is designed to operate in both charging and discharging modes. Fig. 3a displays the charge mode, while the discharge mode is represented in fig. 3b. For the charging (discharging) mode a steam generator (water heater) provides saturated steam (warm water) to the storage module where energy is transferred to (from) the PCM. The storage module provides a mixture of steam and liquid water in an undetermined ratio or steam quality. This water-steam flow is later mixed with liquid water at known temperature and flow. The resulted water-liquid flow and its temperature is measured and the cycle is closed.

During the charge operation saturated steam at 150 °C enters the TES through the A2 conduction (see fig. 2a.) and, once the heat is transferred to the molten salt, saturated water at 140 °C exits the TES module through the A1 pipeline. During the discharge, the operation takes place in the contrary flow direction: saturated water at 130 °C enters the TES through the A1 conduction and, after evaporating in the TES, saturated steam at 130 °C. Tab. 2 summarizes the nominal operation conditions. Here it has been assumed that the pressure drop at the TES is 0.01 MPa.



Fig. 3: Charge (a) and discharge (b) operation mode schemas of the test facility at Plataforma Solar de Almería

Charge mode						
	Temperature [°C]	Pressure [MPa]	Flow [kg/s]	Water phase		
Inlet (A2)	150	0.47	0.04	Saturated steam		
Outlet (A1)	140	0.36	0.04	Saturated water		
Discharge mode						
	Temperature [°C]	Pressure [MPa]	Flow [kg/s]	Water phase		
Inlet (A1)	130	0.27	0.05	Saturated water		
Outlet (A2)	130	0.26	0.05	Saturated steam		

Tab. 2: Nominal operation conditions for the charge and discharge modes at TES module.

## 5. Commissioning of the facility

During the filling of the TES module and the commissioning of the facility significant know-how has been acquired. The most remarkable aspects regarding commissioning of this experimental facility are explained in this section.

## 5.1. Water from the pressure test.

As stated in section 2, the presence of water and oxygen when using Hitec<sup>®</sup> as PCM should be avoided by blanketing the storage module with nitrogen. Blanketing should occur previous to the filling of the storage module with molten salt.

Nitrogen is injected on the top of the module (B2 in fig. 2a), exhausting it through the exit at the B1 connection. Since nitrogen is denser than air, the TES module will remain full of nitrogen when the B1 connection is closed by a screw cap and the upper flange in B2 is removed for the filling of the system.

The TES module should be preheated with steam at 150 °C in order to avoid any plug formation when the molten salt enters the system. During the preheating of the TES module unexpected water steam exhausted through the nitrogen venting system. This water was the remaining of the pressure test performed by the commercial company which sells the module previous to the delivery of the module to PSA and in accordance with the safety procedures any standard equipment that may work under certain pressure should follow. Nitrogen was injected via the B2 inlet (see fig. 2) passing through the complete spiral channel, and forcing the steam to move to the central upper exit B1 (see fig. 4a).

## 5.2. Filling the TES module with molten salt.

The spiral plate internal structure of the TES module makes necessary an external melting of the Hitec® salt previous to the filling of the module. Hitec<sup>®</sup> was melted in a separate furnace, provided with electrical resistances and a control that allows a safe melting of any salt and its release in the TES module. For this purpose, the flange at the top of the TES module was dismounted once the TES module had been innerted with nitrogen, allowing the molten salt charge





Fig. 4: a. Water steam exhausted through the nitrogen venting system. b. Filling of the TES with the external salt furnace.

## 6. Conclusions and future works

Candidate PCMs in the range of 130 °C to 170 °C have been studied. From the most promising ones proposed in the literature, hydroquinone and salicylic acid presented a strong vapor emission upon melting; and D-mannitol displays not only supercooling during freezing, but also a strong degradation after just 50 melting/freezing cycles. The commercial Hitec<sup>®</sup> salt has been selected because of its chemical stability and despite its relatively low enthalpy of fusion.

This salt is very hygroscopic, which can produce a change in the melting temperature, and forces to a previous drying of the TES module and a  $N_2$  blanketing.

Due to the delay caused by the unexpected problems occurred during the commissioning, the expected testing procedure refinement and the evaluation of the thermal behavior are close future activities. The testing procedure to be followed is the one proposed at the SFERA project and named SFERA15T2#1 (*'HTF power curve in discharge/charge'*), case III (Rojas et al., 2011). This procedure allows establishing both discharging and charging curves working at different temperature/pressure pairs. From these curves it is possible to find out experimentally the real Biot number of the storage module, which may be important to validate the simulated behavior of the new design here implemented.

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