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Thermal Energy Storage Materials, Media, and Systems

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JCA Eni ENEA Project: CSP & Thermal Storage

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Abstract. This project is framed within a three-year-long cooperation between Eni and ENEA. It concerns the development of prototypes, technologies, innovative processes, feasibility studies, scenario analysis, exchanging skills, and know-how. This is coherent with the promotion of joint initiatives in the field of energy production, from renewable sources and those with low CO_2 emissions, supercomputing, superconductivity, and circular economy, including innovative processes for waste valorisation and production of biogas, biomethane and biochar. The "CSP & Thermal Storage" has the ambition to exploit solar sources to produce thermal energy according to the energy demand, regardless of the availability of the solar source, through the development of innovative solutions of plants with a programmable production capacity, through the coupling with innovative Thermal Energy Storage (TES) solutions. The objectives of this project are the identification of contexts for using Concentrating Solar Power / Concentrating Solar Heat (CSP/CSH) technology and thermal generation systems coupled to TES, the definition of the "business plan" for the enhancement of these technologies, the identification of partnerships with national and international subjects for the design of industrial solutions in the identified contexts of interest, and the joint participation in competitive tenders through research and development projects that can also lead to the creation, characterization, and validation of prototype units. As for the energy storage, dynamic modelling of the thermocline and Phase Change Materials (PCM) storage systems is also expected, together with a broad-spectrum analysis of possible applications of CSP/CSH coupled with TES along the entire industrial energy supply chain (e.g.: upstream, downstream, power generation). Of particular importance is the development of TES prototypes to be tested on a molten salt-operated circuit integrating two different PCM systems with an Eni proprietary innovative thermocline TES based on concrete, to facilitate the management of the system and to supply high-quality heat to the user. This system consists of a module able to store 40 kWh of thermal energy by phase change materials (PCM), followed by a concrete module of about 150 kWh and another 40 kWh PCM TES with a higher phase change temperature. The overall operating temperature range of the system is 290÷450°C.

Keywords: CSP, TES, Prototype

1. Introduction

In general, in phase change storage systems, the latent heat stored and released by PCMs (Phase Change Materials) is considered a promising candidate for thermal energy storage at all temperature levels. In this case, for the needs of the present project, those having the solid/liquid phase change at medium/high temperatures are useful. The most attractive PCMs have the following characteristics: high energy density, i.e. the ability to accumulate more heat at the unit volume level; abundance in nature; non-toxicity; non-corrosiveness, low cost and high conductivity in solid state. In fact, by using the latent heat of the solid-liquid transition, a large amount of energy can be stored, which can subsequently be released at a nearly constant temperature. Thus, if the user's temperature request allows it, its sensible heat can also be used.

The heat amount, which a PCM can store, due to the contribution of both latent and sensible heat is:

$$Q = m\int_{T_1}^{T_m} c_p(T)dT + m\Delta H_f + m\int_{T_m}^{T_2} c_p(T)dT \qquad (1)$$

where the first term represents the sensible heat exchanged in the solid phase between a generic temperature T_1 and the liquefaction temperature T_m; the second term is the latent heat of fusion, and the third one is the sensible heat exchanged in the liquid phase up to T_2. In the literature, many PCMs are cited in very different temperature ranges and many substances have been studied as potential candidates, but only a few of them are commercialized [1]. All the materials involved in the phase transition could be considered PCMs; however, most of them do not meet the selection criteria required for proper thermal storage in CSP plants. On the other hand, mainly due to the low thermal conductivity of the storage medium, they have lower power outputs, more complex heat exchange systems and higher costs, as well as corrosion problems if the HSM (Heat Storage Material) is chemically aggressive.

Sensible heat TES is the most commercially mature energy storage system, easy to manufacture, based on easily available liquid or solid materials, with good specific heat and thermal diffusivity values, and low cost. On the other hand, these sysyems require large volumes, if the range of initial and final temperature is limited. Nevertheless, sensible heat TESs based on concrete as HSM have the advantage of using widely available, low-cost storage media with a good storage capacity, but their use in TES operating up to about 400 °C require the mix-design and the manufacturing/treatment processes of these materials to be appropriately studied. Given the low thermal diffusivity of concrete, these systems must be modified to promote thermal conductivity, as well as the heat exchange devices appropriately sized [2]. Often, a concrete TES works with a single tank where an HTF (Heat Transfer Fluid) exchanges heat with the HSM within which a thermocline is established. This typical operating mode involves a continuous change in the Heat Transfer Fluid (HTF) temperature at the system outlet during both the charging and discharging phases. It results in a dynamic operation of the Thermal Energy Storage (TES) system and its connected process units. Actually, an “ideal” thermal storage system should have characteristics that belong to one or the other storage technology, such as: high energy density stored, compactness, high efficiency, stable heat temperature supplied, and good power provided during the discharge phase. To achieve this goal, a solution for a hybrid sensible/latent thermal storage system has been proposed and analysed in the literature in which both technologies coexist and contribute to achieve the indicated targets [3-6].

A high-temperature phase change material, specifically the ternary mixture of lithium, sodium, and potassium carbonates, was deemed suitable for this project, taking into account its toxicity, pollution, and corrosiveness profiles [7-10], as well as its stability and phase change temperature. According to literature data [8-10], stainless steel (AISI 304 and 316) can resist the corrosive attack of this mixture, which was confirmed by a specific experimental campaign also extended to AISI 316Ti, AISI321 and Inconel 347. These materials have all shown good specific resistance.

The physical characteristics found in the literature for this mixture are reported in Table 1.

Table 1. *Physical characteristics from the literature of the mixture* Li_2CO_3-Na_2CO_3-K_2CO_3 *(31.1/33.4/34.5 wt%)*

Physical property	Value	Reference
Density (kg/m^3) @450°C	2119	[11]
Specific heat of solid (J/kg/K)	1243	[12]
Specific heat of liquid (J/kg/K)	1453	[12]
Conductivity of solid (W/m/°C)	n.a.	[13]
Conductivity of liquid (W/m/°C)	1.674	[12]
Mean melting temperature (°C)	397	[12-13]
Mean solidification temperature (°C)	387	[12]
Latent heat (kJ/kg)	276	[13]
	229.6/247.1	[12]
Dynamic viscosity (Pa-s) @450°C	$7.15 \cdot 10^{-3}$	[11]

As a low temperature phase change material, the pure salt $NaNO_3$ appears the most appropriate, and it has the advantage of being well known and also used as a mixture for solar salts, at 60 wt% together with KNO_3.

Sodium nitrate, in addition, has also been recently used as PCM by several international research institutes [14-17]. It has a melting temperature of 308 °C. However, it exhibits slight decomposition starting at 380 °C, producing $NaNO_2$ and O_2. This decomposition tends towards equilibrium, especially with air contact, allowing its utilization at higher temperatures, as in this case. Nevertheless, it is advisable not to exceed 600 °C, as significant degradation occurs and physical properties, particularly viscosity and liquefaction, change [11]. On the other hand, carbonate-based TES materials are generally more stable; a limit decomposition temperature under air of 670 °C has been reported [18].

2. Concept

The proposed system involves the creation of a thermal circuit (**Figure 1***a*), equipped with a storage system consisting of two different modules containing phase change materials of approximately 40 kWh each, and a third consisting of a cylinder of homogeneous cementitious material with a series of channels carved internally for the passage of the HTF. It was developed by Eni and it can store, using sensible heat, up to 150 kWh, depending on the difference between initial and final temperature to be adopted (i.e.: 300 °C).

As heat transfer fluid, in order to charge the modules up to a temperature of about 450 °C, the so-called solar salt will be used, i.e., a mixture of sodium and potassium nitrates, already widely used both as HTF and, as HSM, (Heat Storage Material) in various projects.

The latent heat modules are expected to be positioned before and after the Eni-TES: one using a PCM with a phase change temperature at about 300 °C, the other at about 400 °C. Inside the latent heat modules, the heat transfer fluid (solar salts) will flow inside a double spiral heat exchanger, to be used for the energy charge and discharge of the latent heat modules.

The expected experimental tests include both the individual TES modules and all the modules in sequence. In the first case to understand the phenomena that occur in each module, and in the second to delve deeper into the behaviour of the integrated system. To simulate a real system, it will be necessary that, during charging, the Heat Transfer Fluid (HTF) at 450 °C, enters from the side of the PCM with the highest phase change temperature and exits from the side with the lowest. The opposite is in the case of discharging, when the temperature of the HTF, regulated by a fan heater, will be set at 290 °C. **Figure 1***b* shows a rendering of this storage system. It is worth noticing that:

- the buffer tank of the HTF salt is a tank with an integrated pump;
- in the load configuration, the HTF does not pass into the air cooler to avoid unnecessary heat losses, while in the discharge configuration, it still passes into the boiler, which will allow the outlet temperature from the unit heater to be controlled and, if it is lower than the set-point value, to realign it.

Table 2*. Main indicators of the simulations.*

Flow mass (kg/h)	**250**	**400**	
Charging time (h)	>12		at 98% of charged energy
Discharging time (h)	>12	>12	at 98% of charged energy
Theoretical capacity (kWh)	158	158	
Charged energy (kWh)	91	127	discharged energy after 6 h
Discharged energy (kWh)	89	122	charged energy after 6 h
Utilization Factor (%)	56.3	77.2	
Thermal efficiency (%)	97.8	96.1	after 6 hours

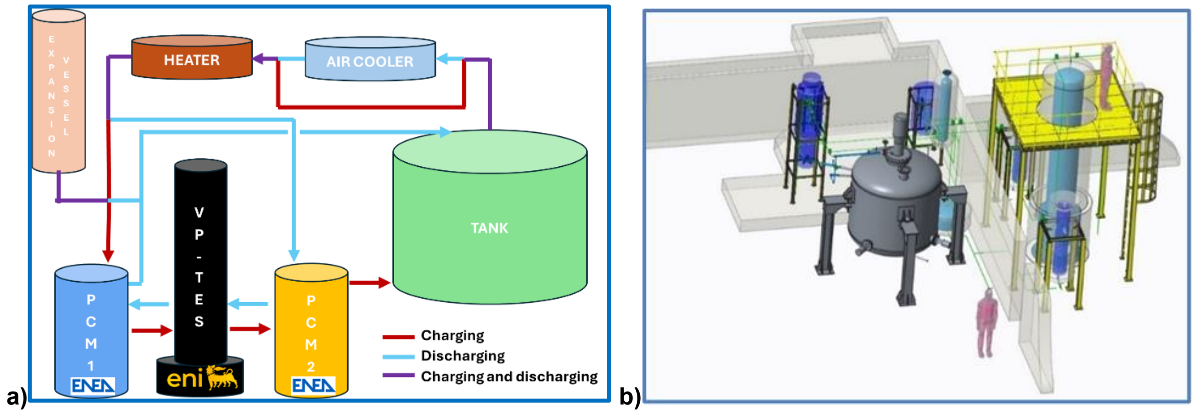

Figure 1*. a) Concept and b) rendering of the demonstrative plant*

More specifically, in charging, the solar salt coming from the storage tank heats up to the desired temperature in the boiler, enters the modules containing PCM1, Eni-TES (also called VP-TES) and PCM2 and then comes back to the tank. Initially, the molten salt will find preheated modules, at 290 °C, and will therefore begin to load them. However, while the first module begins to load, the remaining modules will remain at the same temperature until the salt absorbs and releases enough heat to reach an equilibrium. This heat will then begin to warm the second module, followed by the third, until they are fully charged. Similarly, but with reverse circulation and by passage through an air-cooler and a boiler in the discharge case.

Table 2 provides a summary of indicators evaluated in the preceding simulations to assess system performance. These indicators are: theoretical capacity (the inherent heat storage capability of the material, here assessed without considering insulation, heat transfer fluid, or containment material, and within a 160°C temperature range); the utilization factor (the proportion of the theoretical capacity that is actually discharged); and thermal efficiency (the rate between discharging and charged energy). The 6-hour period considered in some calculations is relevant for Concentrated Solar Power (CSP) applications.

3. Simulation results

A numerical simulation of the thermal behaviour of a "cascade" system consisting of the above-mentioned three thermal storage elements was performed (**Figure 2**). The temperatures in the arrows concern thermal oil at the start of the charge and discharge, when the system is at the minimum and maximum operative temperature level, respectively. The temperature in the PCM blocks corresponds to the phase change.

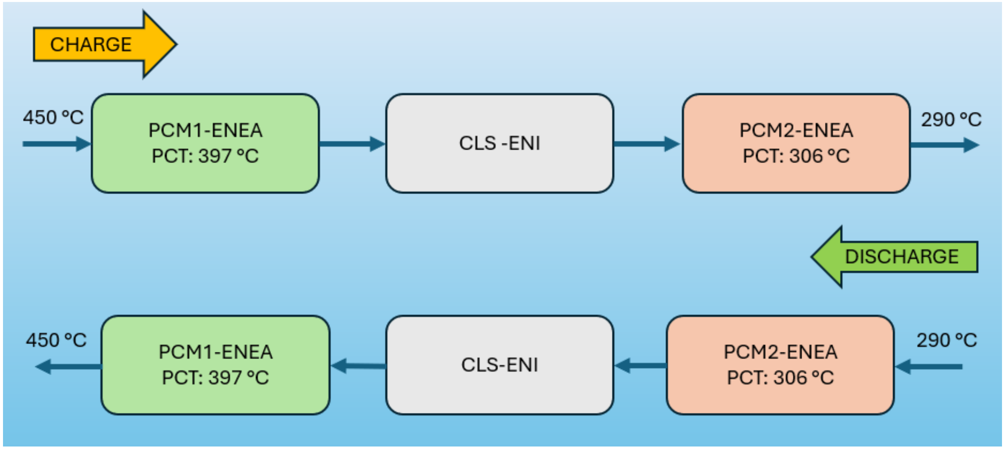

Figure 2*. Schematic of the use of a cascade TES prototype for the loading and unloading phases*

In each charge and discharge cycle, the simulation was carried out in three steps, one for each storage element. At the inlet of each element, the mass flow rate of the HTF remains the same while its temperature will be equal to its previous element outlet, except for the first of the series since it is the entrance to the system. It appears that:

In charge:

- The PCM1 element (PM1) has a rather long melting phase, about 7 hours, in which it maintains an HTF outlet temperature close to 425 °C. Then, it rises, reaching 450 °C within 12 hours. The charging time is about 8 hours.
- The thermocline concrete element (CLS) has an HTF outlet temperature that starts to rise after about 3 hours and slows down after 8 hours. At the end of the simulation (12 hours) it reaches a temperature of about 425 °C.
- The PCM2 element (PM2) has an exit temperature that rises quickly between 3 and 5 hours, reaching 330 °C, then slows up to 7.5 hours, at about 360 °C. Afterwards, it rises and after 12 hours reaches 420 °C, with a load factor of 87%.

In discharge:

- The element with PCM2 has a very fast initial HTF outlet temperature drop, up to 4.5 hours. It stays constant for the rest of the simulation at around 300 °C.
- The concrete element has an HTF outlet temperature that starts to drop after around 2.5 hours, first quickly and then more slowly. At the end of the simulation (12 hours) it reaches a temperature of around 300 °C.
- The element with PCM1 has an outlet temperature that drops fast between 3 and 6 hours. Afterwards, it slows down and gradually drops from 400 °C to 380 °C, up to 9.5 hours. Finally, the temperature drops quickly, reaching around 310 °C after 12 hours.

The above results refer to a flow rate of 400 kg/h. If the flow rate drops to 250 kg/h the dynamics is strongly slowed. In both cases, the mass flow of the HTF is in the laminar range.

Figure 3 shows the above-mentioned behaviour: the black lines describe the inlet HTF temperature, while the coloured ones define the temperatures of the HTF exiting the corresponding module.

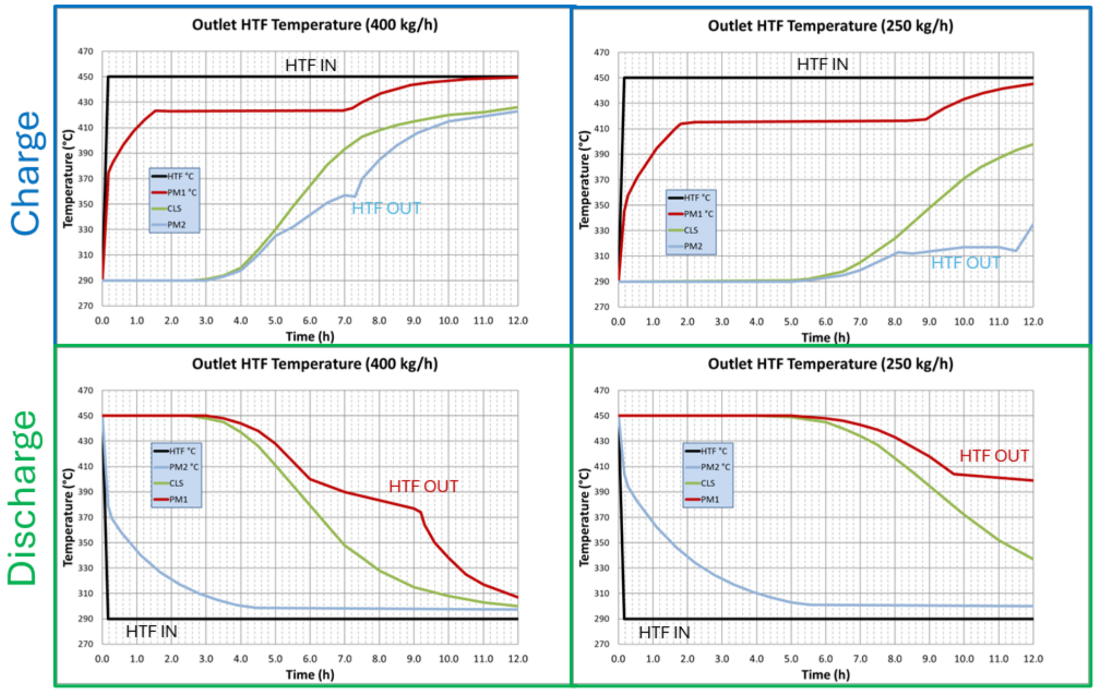

Figure 3. *Behaviour of the HTF outlet temperature from each module, during the charge and discharge steps of a cascade TES prototype. HTF OUT: system temperature outlet.*

In summary, the first evidence is about the way as the two LHTES (Latent Heat TES) systems placed upstream and downstream of the thermocline module manage to stabilize the HTF outlet temperature for a few hours. In charge, using a flow rate of 400 kg/h, the LHTES with the PCM2 manages, between the fifth and eighth hour, to maintain the outlet temperature below 370 °C. If the flow rate is lower (250 kg/h) this effect is prolonged (up to and beyond the eleventh hour) and increased (temperature below 310 °C). Conversely, in discharge, using a flow rate of 400 kg/h, the LHTES with the PCM1 manages, between the sixth and ninth hour, to limit the outlet temperature above 380 °C. If the flow rate is lower (250 kg/h) this effect is prolonged (between the fifth and twelfth hour) and increased (temperature above 400 °C). Of course, these effects are positive both to simplify the management of the system and to provide high-quality heat to the user. On the other hand, such a high thermal capacity requires very long charge/discharge times.

3. Conclusions

The project here shortly discussed consists of the realization of a thermal circuit equipped with a storage system using two different modules including phase change materials, and one of consisting of cementitious material. Since the storage temperatures can reach 450 °C, the heat transfer fluid to be used for charging and discharging the modules will be the so-called solar salt. The development of such a high-temperature TES (Thermal energy Storage), will allow testing two important aspects:

- integration of a thermocline cementitious module with two different kinds of PCM;
- performing experimental tests on cement materials at a temperature of about 400 °C in contact with molten salts.

The effects highlighted by proper simulations are positive both to facilitate the management of the system and to provide high-quality heat to the user, and are closely linked, in addition to the mass flow rate of the heat transfer fluid, to their high thermal capacity. On the other hand, such a high thermal capacity requires very long charging/discharging times to be evaluated, based on the kind of application. Furthermore, the slow charge or discharge of the storage elements also implies an evident difficulty in exploiting the thermal capacity, especially for the cementitious material and for $NaNO_3$.

The test execution methods, once the system has been built, include both tests of the individual TES modules and of the same modules in series. In the first case, to understand the phenomena that occur in each module, and in the second one to delve deeper into the behaviour of the integrated system. To simulate a real system, it will be necessary that, during charging, the HTF, at 450 °C, enters from the side of the PCM with the highest phase change temperature and exits from the one with the lowest. The opposite, in case of discharging, when the temperature of the HTF, regulated by a fan heater, will be set at 290 °C.

Author contributions

Liberatore Raffaele: conceptualization, project administration, writing – original draft; Nana Francesca: supervision, project administration, writing – review and editing; Cardamone Stefano: investigation; Passera Tamara: investigation; Carnelli Lino: supervision, investigation; Russo Valeria: formal analysis; Miliozzi Adio: data curation, formal analysis; Nicolini Daniele: data curation; Petroni Giuseppe: data curation; Gaggioli Walter: formal analysis, funding acquisition, methodology.

Competing interests

The authors declare that they have no competing interests.

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