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# Experience from Commissioning Tests on ENEA's Thermocline Molten Salt/Pebbles Pilot Plant

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**Abstract.** The blast furnace slags are a by-product of the production process of cast iron, during which large amounts of liquid slags are formed. The composition of the blast furnace slags depends on the actual quality and proportion of the minerals and fluxes present in the blast furnace charge. Every year the steel industry in Europe produces 2900 tons of slags that, if left untreated, represent an industrial waste to be sent to landfills with serious environmental impact. In the RESLAG (Turning waste from steel industry into valuable low cost feedstock for energy intensive industry) project, the use of waste products deriving from iron and steel plants as new feedstock in different fields is considered: recovery of precious metals, thermal energy storage systems for steel-making and CSP industry, production of innovative refractory ceramic compounds. Within this framework, ENEA is investigating the possibility of using pebbles made with slags produced by the steel industry as a filler in high-temperature packed-bed thermocline TES systems, using a binary mixture of molten salts (60% $NaNO_3$ 40% $KNO_3$) as HTF. More specifically, the pebbles are obtained by processing and sintering Electric Arc Furnace (EAF) slags produced during the manufacture of crude steel. Here, the lessons learned and the first experimental results collected during the commissioning phases of the PBTTES pilot plant developed within the RESLAG project are reported. In particular, the paper firstly reports about a preliminary set of tests carried out to check the chemical compatibility of the slags with the molten salts. Subsequently, the pilot plant is described and the results of the first commissioning tests, which were aimed at flooding the packed-bed with molten salts and checking the installed instrumentation, are reported.

## INTRODUCTION

The integration of a thermal energy storage (TES) system in a concentrated solar power (CSP) plant can greatly improve its performance, offering an enhanced behaviour. TES plays a crucial role in the ability of the CSP plant to store and manage the thermal energy in such a way to allow dispatchable production, increase the capacity factor of the plant and, in the end, reduce the cost of production of power. Currently, the development of new efficient and cost-effective TES solutions is a very important goal pursued by several research centers worldwide. In this respect, different TES concepts are explored with the aim of developing customized solutions for specific CSP applications. Among the different options considered, packed-bed thermocline TES (PBTTES) systems are currently object of a significant interest [1-5]. These sensible-heat TES systems exploit the presence of an axial temperature gradient to store the hot and cold heat storage medium (HSM) within a single tank. The HSM consists in part in a packed-bed of inert and inexpensive solid, through which the heat transfer fluid (HTF) is flowed. During the TES charging phase, the hot HTF coming from the solar field is fed from the top of the packed bed and progressively heats the solid up while flowing from top to bottom through the packed bed. During the discharging phase, the cold HTF coming from the power block is fed from the bottom of the packed bed and the mass and heat fluxes are reversed.

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By using a single tank and replacing a part of the liquid HSM with an inexpensive solid (e.g., derived from industrial waste), PBTTES can potentially achieve lower costs compared to conventional 2-tank TES solutions using molten salts as HSM [3,4]. However, in PBTTES systems the HTF flows through and comes into direct contact with the HSM and, as a consequence, the chemical compatibility between such materials is a crucial feature that must be ensured to avoid safety and operating issues. This is true both for systems using gaseous HTFs (e.g., air), in which, for example, humidity in the gas may cause swelling and breakage of the solid particles, and, to a much larger extent, for systems using molten salts as HTF. Indeed, molten nitrates are strong oxidants and react with a variety of compounds, also leading to the decomposition of the salts and gas formation; furthermore, the products of such reactions or the release of components from the solid may alter the molten salt composition and increase corrosion risks. In this respect, steel slags are complex mixtures including numerous components with a variable composition; therefore, compatibility issues must be assessed with care.

The use of industrial waste in PBTTES systems is within the scope of the European project RESLAG [6]. Such project aims at developing solutions for the valorization of steel slags through 3 eco-innovative industrial alternative applications that are proved in 5 demonstration pilots. The RESLAG project proposal is aligned with the challenges outlined in the call WASTE-1-2014: moving towards a circular economy through industrial symbiosis. In particular, one of the tasks of the project is to assess the technical feasibility of using steel slags as HSM in PBTTES systems for CSP plants using molten salts as HTF. The slags are used in the form of pebbles produced by Optimum Cement (France) according to a sintering process defined within the project, which is beyond the scope of this paper.

The slag pebbles are tested in a pilot plant built at ENEA Casaccia Research center (Rome, Italy) that includes a test section where the thermo-fluid dynamic conditions (i.e., flow pattern, superficial velocity, inlet temperatures) occurring in an industrial PBTTES system are reproduced at a smaller scale. The operating conditions considered correspond to those occurring in a central receiver CSP plant using molten salts as HTF (temperature range approximately 300-560 ºC). Other pilot-scale PBTTES systems using molten salts as HTF have been previously built [5,7], but this facility is the first on using sintered slag pebbles as HSM.

In this paper, the information collected prior to and during the commissioning phase of the PBTTES pilot plant developed within the RESLAG project are reported. In particular, the paper firstly reports about a preliminary set of tests carried out to check the chemical compatibility of the slags with the molten salts. Since transformation of nitrates to nitrites in the salt and migration of iron, calcium and silicon cations from the slag to the salt are reported in the literature for raw slags [8], specific tests were carried out in order to evaluate the compatibility between the sintered slags and the HTF employed in the demonstrator, i.e. a mixture of $NaNO_3/KNO_3$ 60/40 wt% ("solar salt"). It is worth noting that only chemical aspects are considered in the characterization of the slags reported here; the thermophysical properties were determined within the RESLAG project and previously reported in the literature [4]. In the second part of the paper, the pilot plant is described and the results of the first commissioning tests, which were aimed at flooding the packed-bed with molten salts and checking the installed instrumentation, are reported.



## COMPATIBILITY TESTS BETWEEN THE SINTERED SLAGS AND THE "SOLAR SALT" AT 550°C IN STATIC CONDITIONS

The tests were carried out in a stainless-steel autoclave (SS 304) inserted inside a heating system, in which slag samples were immersed into liquid solar salt. The top of the autoclave was closed with a flange, which presented two connectors, a first one for carrier air inlet and a second one for the outlet of the produced gases. During each experiment, chromatographic air ($O_2/N_2$ with a volume ratio of 20/80) was continuously flowed through the vessel headspace at 5 Nml/min, by using a Bronkhorst mass flow controller. The flow rate of the outlet stream was measured with a mass flow meter (Bronkhorst) in order to check the amount of produced gases and the composition was analysed with a MicroGC (Varian 4900, MS5 10 m column). The tests were carried out at a constant temperature of 550 °C, which is the maximum operating temperature of the pilot plant and in line with the maximum temperature in CSP plants using molten salts as HTF.

Two different batches of sintered slag samples, hereafter indicated as "type I" and "type II", were used in the tests. Both types consist of a mixture containing metal, nonmetal and mixed oxides. In order to obtain an indicative composition, an elemental analysis was carried out. At this purpose, samples from both batches were crushed, dissolved in boiling aqua regia, and analyzed by a microwave plasma instrument (MP-AES 4100). The results, which are similar for both batches, are reported in Tab. 1 as weight percentages.

Two different tests were carried out with different types of slag samples. In a first experiment (test I), 1 kg of molten solar salt was contacted with 523 g (four samples) of a first batch of cubic samples of type I slags for about

450 h; in a second test (test II), 750 g of solar salt were contacted with about 140 g of type II sintered slags (37x27x18 mm pebbles) for about 750 h. A summary of the tests performed is reported in Table 2.

At the end of the tests, the flange was removed and the autoclave was emptied. Both the slags and the nitrate mixture were cooled down, weighed and examined to assess the transfer of metal from slag to “solar salt”. To that end, some samples of the slags were crushed, dissolved in boiling aqua regia, and analyzed for elemental composition by a microwave plasma instrument (MP-AES 4100). The same operation was also carried out with samples of slags not used in the experiment. The molten salt was dissolved into deionized water, and titrated with HCl, in order to detect the presence of alkaline or alkaline earth oxides. Other molten salts samples were also analyzed with ICP. Figure 1 reports the oxygen and nitrogen production over the test time for the two types of slag analyzed. In both cases, after a low initial production of nitrogen and oxygen, outgassing from the liquid drops to zero.

**TABLE 1.** Elemental composition (weight percentage) of the slags used in the compatibility tests.

| | **Al** | **V** | **Cr** | **Mn** | **Fe** | **Co** | **Ni** | **Cu** | **Zn** | **Cd** | **Sn** | **Pb** | **Na** | **K** | **Ca** | **Mg** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Type I | 3.5 | <0.3 | 0.66 | 2.89 | 27.5 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | 0.58 | 0.73 | 15.5 | 6 |
| Type II | 2.8 | <0.3 | 0.7 | 3.1 | 33.2 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | 15.1 | 6.9 |

**TABLE 2.** Summary of the compatibility tests carried out.

| **Parameter** | **Test I** | **Test II** |
|---|---|---|
| Type of slag | I | II |
| Shape of slag samples | Cubic | Pebbles |
| Mass of slags | 523 g | 140 g |
| Mass of solar salt | 1000 g | 750 g |
| Temperature | 550 °C | 550 °C |
| Duration | 450 h | 750 h |



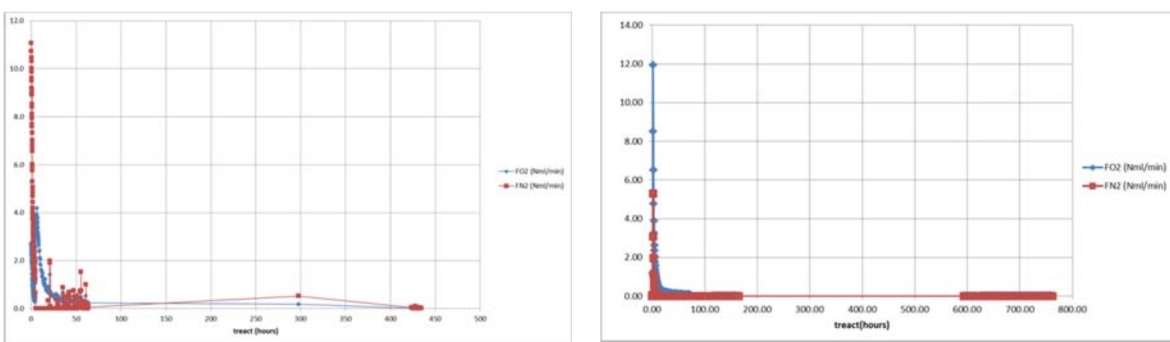


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**FIGURE 1.** Oxygen and nitrogen production over the test time a: slag type I, b slag type b.

No significant weight change was observed for both the slags and the melt during the tests. Furthermore, it was possible to measure the presence of oxides and metals with high accuracy and no metal (according to the detection limit) was leached into the solar salt; also, practically no sodium or potassium oxides were detected in the melt.

Based on the evidence reported above, it was concluded that, under static conditions, the slags proved stable in contact with the solar salt at 550 °C. The slag pebbles were used in the PBTTES pilot system.

# DESCRIPTION OF ENEA'S THERMOCLINE MOLTEN SALT/PEBBLES PILOT PLANT

The test section of the pilot plant consists of a cylindrical tank (inner diameter 1 m and height about 4.5 m) appropriately designed for research purposes (see Figure 2). The fixed-bed made with slag pebbles (3 m height) is placed inside the tank, between two distribution plates. During the charge phase, the molten salt flow through the packed from top to bottom: the salts are fed through a pre-distributor that ensures uniform distribution of the flow across the tank cross section in a small liquid volume above the packed-bed; the salts then flow by gravity through the packed-bed after crossing a sieve plate distributor that further ensures flow uniformity. During the discharge phase, the molten salts are fed from a nozzle located on the center of the dished end on the bottom of the tank and flow across a sieve plate that acts both as flow distributor and support for the packed-bed; the salts are then collected in the upper part of the tank after crossing a weir that ensures a constant liquid head of 40 cm above the packed-bed. The storage inventory (only pebbles of slags) loaded during the commissioning of the system is about 4140 kg. The main packed-bed parameters are summarized in Table 3.

**TABLE 3.** Packed-bed geometry specifications of the PBTTES pilot system.

| | |
|---|---|
| Height | 3 m |
| Diameter | 1 m |
| Void fraction | 0.38 |
| Slag mass | 4140 kg |

The pilot plant includes the experimental mock-up of the TES system (test section) and other components, within a molten salt loop integrated with the ENEA PCS facility. The other key components are the pumping tank, an electric heater and an air cooler. The pumping tank has a threefold purpose: it hosts the pump used to circulate the molten salt stream in the circuit, acts as a thermal buffer to reduce the maximum heating/cooling power required at the heater/cooler during the charge/discharge tests and also serves as vessel for molten salt collection when the circuit is drained. The flow diagram and the main instrumentation of the circuit is shown in Figure 2a, where blue and red arrows highlight the fluid flow directions during the discharge and charge phases, respectively.

The thermocline tank is equipped with an electrical tracing system composed by three electrical mineral cables placed in direct contact with the external wall of the tank and protected from the external insulation of the tank with a 0.5 mm thick stainless-steel sheet. The electrical tracing system is supplied by an electrical power supply unit (three phases, 20 kW). The power of each phase is regulated by the Digital Control System of the plant on the base of a PID algorithm that employs the average wall temperature as controlled variable.



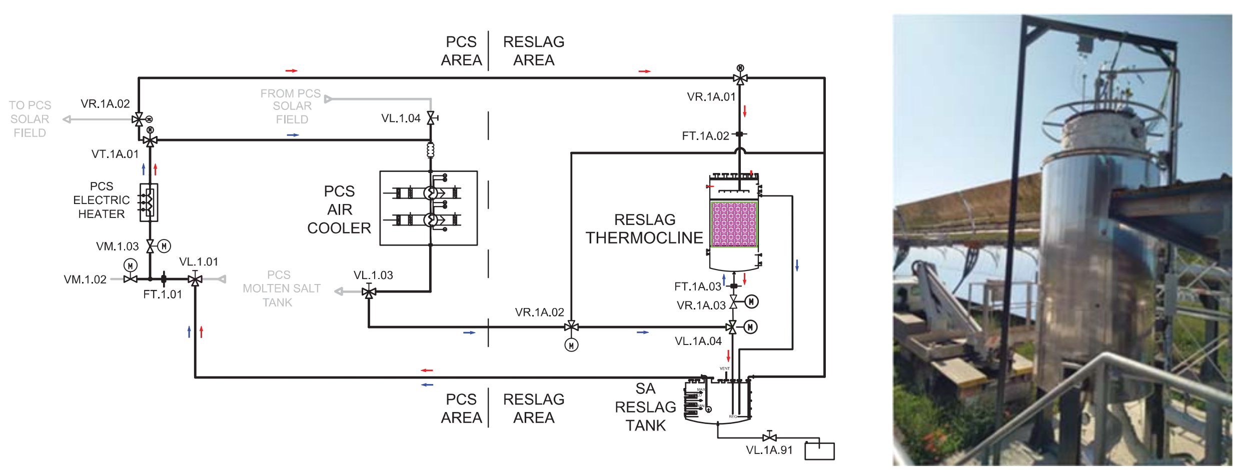


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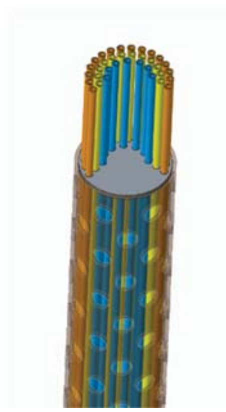
**FIGURE 2.** PBTTES pilot plant: a) Flow diagram of the RESLAG/PCS circuit (red arrows: flow direction during the charge phase; blue arrows: flow direction during the discharge phase; grey: connections with the PCS plant); b) External view of the test section.

The distribution of the temperatures inside the fixed bed is measured through the use of type K thermocouples having an accuracy class of 0 (calibrate in four points in the range 290 - 550 °C).

The distribution of the thermocouples is as follows: the temperature is measured every 0.2 m along central axis of the packed bed, starting from a distance of 0.1 from the top and bottom sections of the packed-bed (15 thermocouples) and in other 8 points of the packed bed. Furthermore, additional thermocouples are placed on the external wall of the test section (one every 0.25 m).

The thermocouples are inserted in the packed-bed from the top by using well probes (see Figure 3), consisting in a cylindrical perforated wall containing a bundle of thermocouples. Each thermocouple has a different length, in order to reach different depths in the bed according to the spatial distribution described above. The perforated wall protects the thermocouples when the packed-bed is loaded in the tank, while allowing the molten salts to come into direct contact with the hot junction of the thermocouple. Transversal baffles placed inside the well serve as guides for the thermocouples and prevent molten salts from flowing axially within the well.



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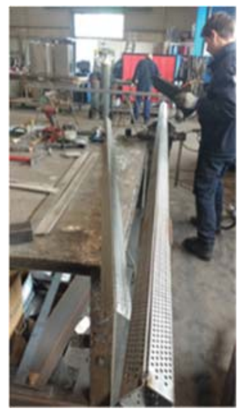


b

**FIGURE 3.** Temperature well probes: a) 3D rendering of a probe section, b) Perforated walls being shaped.



## COMMISSIONING TESTS

After the construction of the facility was completed, commissioning tests were carried out in order to ensure that all the components and automatic controls were correctly working and the plant could be operated as expected during the different types of tests to be carried out. In this phase, molten salts were kept at an approximatively constant temperature between 300 and 310 °C and flowed in the different parts of circuit with a total flow-rate from 3 to 6.5 kg/s. Such flowrates exceed the maximum design flowrate of the pilot TES unit, because, during operation, only a variable fraction of the total pumped flow is fed to the test section, while the remaining part is directly recirculated to the pumping tank. This is required in order to use the electrical heater and air cooler of the PCS facility; whose minimum operating flowrates exceed the operating range of the pilot TES unit.

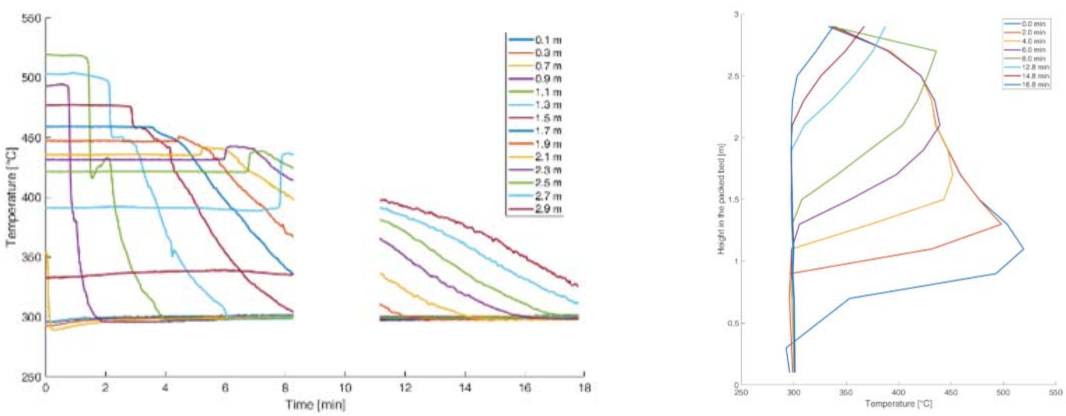
After checking the correct flow of molten salts in the charging and discharging modes, while still keeping the test section by-passed, the first filling of the test section with molten salts was carried out. Before that, the temperature of the packed-bed was raised above 300-310 °C by using the electrical tracing of the TES tank: this first step was required not only to prevent salt freezing in the packed bed, but also to test the response of the thermocouples placed inside the packed-bed in a condition similar to those of discharging tests. The temperature profile within the packed bed at the end of this pre-heating phase can be seen in Figure 4b. The profile is not uniform, with temperatures exceeding 500 °C in the central part and temperatures approaching 300°C in the uppermost and lowermost layers of the packed-bed. This is due to the higher rate of heat loss through the upper and lower surfaces of the packed bed and to the pre-heating operation being stopped when the average temperature in the packed-bed was significantly higher than 300°C (which is sufficient for thermocouple testing) rather than waiting for heating completion.

Molten salts were fed to the bottom of the pre-heated TES tank with a flowrate of about 2.7 kg/s (total circulating flowrate: 3.4 kg/s). The trends of the temperatures measured by the thermocouples placed on the packed-bed axis are reported in Figure 4a. It can be seen that all trends are consistent with the initial temperature profile, feed temperature and axial position of the thermocouples: all the temperatures evolve from their initial value to the temperature of the feed as the molten salt free surface moves upward through the packed-bed. The delay in cooling is clearly due to the heat capacity of the solid. Jumps in the thermocouple readings in Figure 4a allow to follow the liquid level in the tank during the filling operation and show that the tank is fully flooded in about 10 min, which is consistent with the flowrate used and void fraction of the bed; it is worth noting that this is the liquid residence time in the tank (at the conditions of this test) and not the thermal discharging time. No other means of measuring the liquid level within the packed bed is envisaged, while an ultrasonic sensor allows to check the liquid level in the weir in the upper part of the tank, when the packed-bed is fully flooded. The evolution of the axial temperature profiles in the packed-bed during the filling operation is reported in Figure 4b. No significant radial temperature gradients were observed during this phase.

With the filling operation, the experimental facility is fully commissioned and ready for the experimental campaign.

## CONCLUSIONS

The commissioning of a new PBTTES pilot plant has been successfully completed at the ENEA Casaccia Research Center within the framework of the RESLAG project. The plant uses a packed bed of pebbles made with recycled sintered steel slags as HSM and molten salts (solar salt) as HTF. This new facility will allow to characterize the thermo-fluid dynamic behavior of this type of TES systems under realistic operating conditions and on a significant scale. The compatibility of the solid filler with the molten salts was proven with specific tests before the construction of the pilot plant; however, the future experimental campaigns on the pilot will also allow to assess other operating issues related to the packed bed like particle breakage, release of powders in the molten salt stream and, if necessary, evaluate appropriate countermeasures.




(a) (b)

**FIGURE 4.** Temperature profiles during the commissioning test of the PBTTES pilot plant: (a) time-course of the temperatures on the tank axis at different axial positions; (b) evolution of the axial temperature profiles in the packed bed.

## LIST OF ACRONYMS

| | |
|---|---|
| GC | Gas cromatograph |
| HTF | Heat transfer fluid |
| HSM | Heat storage material |
| ICP | Inductively coupled plasma |
| PBTTES | Packed-bed thermocline thermal energy storage |
| TES | Thermal energy storage |

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