

Investigation of the long-term stability of quartzite and basalt for a potential use as filler materials for a molten-salt based thermocline storage concept

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ABSTRACT

Solar thermal power plants with integrated thermal storage are candidates for renewable energy production concepts. For cost reduction of thermal energy storage a single tank concept, the so called thermocline storage concept, instead of the two-tank molten salt thermal storage is as promising cost reduction option. Further cost reductions in the thermocline storage are expected by replacing a significant amount of Solar Salt by a low cost filler material. Such filler materials have to be stable in molten salt at temperatures up to 560 °C. In this work degradation studies on quartzite and basalt types in molten salt are carried out after a preselection has been published elsewhere recently. The investigations are focused on the compatibility of natural stones with Solar Salt, a mixture of sodium nitrate and potassium nitrate, as common heat storage material.

This work addresses changes of the molten salt properties and in the microstructure of the natural stones depending on the exposure time in molten salt at temperatures of approximately 560 °C. In the first step of the material investigation the natural stones were isothermally stored in Solar Salt at a maximum temperature of 560 °C for up to 10.000 h. After the thermal treatment the microstructure of the stones was investigated by QEMSCAN (Quantitative Evaluation of Minerals by Scanning electron microscopy). By means of this analysis method the changes in the microstructure of quartzite and basalt was detected and arising stone components are identified. The melting temperature and enthalpy of Solar Salt was measured and compared with the salt properties before the thermal treatment. Additionally, the specific heat capacities of basalt and quartzite depending on the temperature were determined. The results are essential to verify the suitability of quartzite and basalt as potential filler materials in modern thermocline storage concepts.

1. Introduction

1.1. Thermocline storage concept

Two-tank molten salt storage systems mark the current state-of-the-art for thermal energy storage (TES) in parabolic trough and solar tower power plants (Gil et al., 2010). In general, the two-tank storage system consists of two separate storage tanks, one operating at a higher temperature level (hot tank) and the other one at a lower level (cold tank). During charging, salt is extracted from the cold tank, heated to a higher temperature and subsequently stored inside the hot tank. The method of heating the salt distinguishes the two tank system into two concepts. In direct systems, the molten salt is directly heated inside the collectors of a parabolic trough power plant or inside the receiver of a tower power plant. Thus, molten salt and heat transferring fluid (HTF) in the plant are the same. In indirect systems, the HTF is different from the molten

salt used in the storage system. A common example is the parabolic trough system with thermal oil, where the heat must be transferred from the oil to the salt through a heat exchanger.

To discharge the storage system, the charging process is reversed: In the direct system, molten salt can be extracted from the hot tank, fed into the steam generator and eventually stored inside the cold tank. In indirect systems an intermediate step is necessary, where the heat is first transferred to the HTF, which then transfers the heat to the steam generator.

One drawback of the two-tank concept is the poor utilization of the available volume of the tanks. For example, at the beginning of the storage process, the cold tank is filled with salt whereas the hot tank must be empty to store the hot molten salt. Hence, only 50% of the available space is used.

The thermocline concept aims for further cost reductions in molten salt sensible heat thermal energy storage systems, by using only a single

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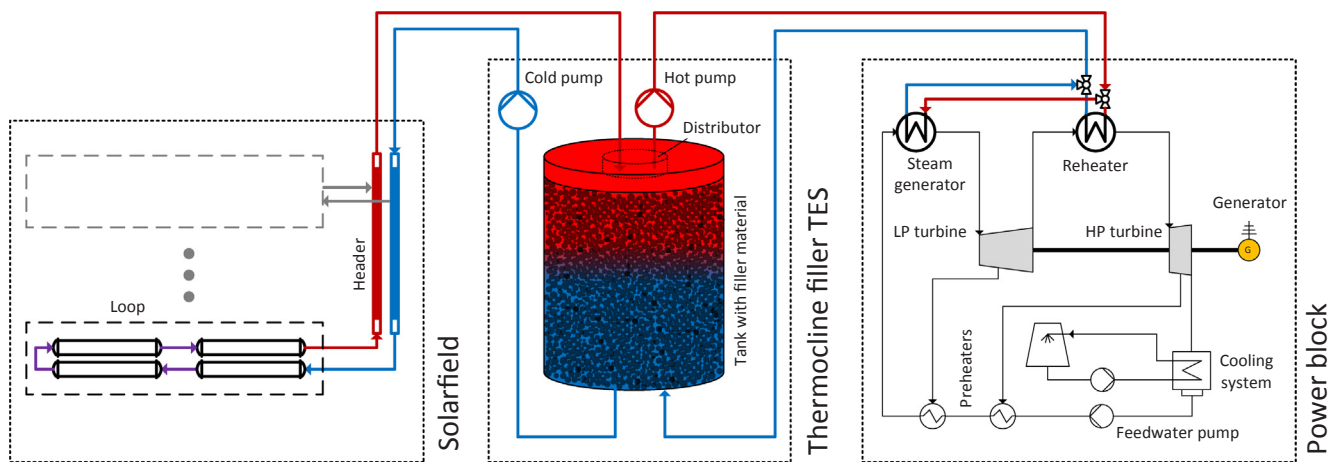


Fig. 1. An illustration of the thermocline storage tank in a solar trough power plant.

tank for storing molten salt (Libby, 2010). The working principle is illustrated in Fig. 1 and differs from the two-tank system. To charge the thermocline storage, cold molten salt is extracted from the bottom of the tank and, after heating by the HTF, returned at a higher temperature level at the top of the tank. Due to the salt's lower density at higher temperatures, it remains stratified and does not mix with the colder salt. For discharging the process has to be reversed. With this technology, costs for foundation, tank material and piping of the cold molten salt tank can be reduced significantly (Libby, 2010).

A vast potential for further cost reduction is the use of cheap filler material. For this concept, a low cost filler material is embedded in the storage tank, replacing Solar Salt. Whilst at the time of writing, costs for molten salt lie in the range of 500–1000 €/t, filler materials – such as basalt – are as low as 50 €/t and their volumetric heat capacity is comparable to that of molten salt (Martin et al., 2014). Although utilization of these systems is a little lower due to limited heat transfer between filler and molten salt, the overall cost reduction potential can be up to 40% (Libby, 2010).

The thermocline concept was first demonstrated by Sandia (Faas et al., 1986). The investigated thermocline storage was the largest system to date and part of the Solar One power plant with 170 MWh_{th} capacity. As filler material granite rock and as HTF thermal oil (Caloria HT-43) was used, which limited the operation temperature to 300 °C. Besides the storage system itself, chemical and mechanical stability have been investigated as well. The largest system using molten salt has also been built at Sandia (Pacheco et al., 2002). The authors presented results of a 2.3 MWh_{th} storage module with a maximum operation temperature of 400 °C. Another mid-sized thermocline system based on thermal oil with 350 °C temperature has been investigated at CEA (Bruch et al., 2014). Later CEA presented a 30 m³ thermocline storage system, as part of a small ORC Fresnel power plant with an operating temperature of 300 °C. The storage system uses thermal oil and unclassified rock as filler material (Rodat et al., 2015). A smaller experiment with rapeseed oil/quartzite rock and 8.3 kWh_{th} has been recently presented by PROMES-CNRS (Hoffmann et al., 2016). Gil et al. (2010) presented an overview of the research activities to the thermocline storage concept with one single tank for molten salt storage instead of two tanks.

At the DLR site in Cologne, a thermocline test facility with 22 m³ storage volume has been installed and is now in the commissioning phase (Odenthal et al., 2017). An illustration of the storage volume is shown in Fig. 2. Each component is equipped with electric trace heating to minimize heat losses to the environment. This is particularly advantageous for the storage volume which can thus be considered adiabatic. Inside the storage volume 150 thermocouples measure the three-dimensional temperature field. The filler material is held by a stack of three removable baskets. Through this design, test

arrangements can be prepared on the outside and later inserted into the storage tank. Hot and cold molten salt is provided by two reservoir tanks, whose temperatures can be individually adjusted. These reservoirs imitate the behavior of attached energy sources or sinks (i.e. heater, solar collector or power plant). The pumps are designed for a molten salt mass flow of more than 14 tons/h at 560 °C.

The operation of the TESIS plant, and other thermocline systems in general, works as follows: During discharging, cold salt flows into the storage volume at the bottom and flows through the filler material up to the top, where it is extracted from a pipe attached on the side. Heat is transferred from the hot filler material to the initially colder molten salt. The heat transfer is usually limited to a region between already cooled and yet hot filler material, which is called the thermocline zone. This thermocline zone slowly moves through the storage volume until it reaches the top. At this point, the exit temperature of the hot salt will decline, having negative effects on the power unit attached to the storage system. Hence, a thin thermocline zone is favorable, keeping the exit temperature at a constant level for as long as possible. Previous publications dealing with the optimization of thermocline systems confirm that the operation strategy significantly affects the shape of the thermocline zone and eventually influences the thermal behavior of such thermocline systems (Bayón and Rojas, 2013).

Looking at recent theoretical publications, it can be noted that focus lies either on more specific effects or system simulations. One of the more specific topics is the effect of thermal ratcheting which has been addressed by CEA (Sassine et al., 2016), Sandia (Kolb et al., 2011), at Purdue University (Flueckiger et al., 2013) and ETSEIAT (González et al., 2015). The effect is caused by a thermally expanding storage vessel which might cause the packing to collapse. When the vessel is cooling down during discharging, its contraction is inhibited by the packing, causing mechanical strain. However, most publications could not find signs of ratcheting but state that at higher temperature different scenarios might occur.

Chang et al. (2016) investigated the impact of modifications of the inner tank walls on the thermal performance of thermocline storage tanks. Gaggioli et al. (2015) presented a molten salt storage system with an embedded heat exchanger for steam production. This embedded approach promises cost reductions and a better thermal stratification.

EPRI and Sandia carried out a comprehensive study, where the thermocline concept was compared to the two-tank system for various power plant design cases (Libby, 2010; Kolb et al., 2011). The study uses a power block in TRNSYS and a cost model to evaluate specific costs from annual simulations. At CIEMAT and the Cyprus Institute preliminary research has been conducted to model thermocline behavior with analytic functions (Bayón and Rojas, 2014; Votyakov and Bonanos, 2015). Later these models have been used to study operation strategies for solar thermal power plants with thermocline storage

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