THERMAL ENERGY STORAGE IN MOLTEN SALTS: OVERVIEW OF NOVEL CONCEPTS AND THE DLR TEST FACILITY (TESIS)

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(1) Introduction

At present, two-tank molten salt storage systems are the established commercially available concept for solar thermal power plants. Due to their low vapor pressure and comparatively high thermal stability, molten salts are preferred as the heat transfer fluid and storage medium. However, due to pricing pressure, the development of alternative, more cost-effective concepts is an important step in making thermal energy storage more competitive for industrial processes and solar thermal applications[1]-[2]. A closer look at the capital cost distribution of two-tank storage systems, reveals that indirect systems with a maximum operating temperature of 400 °C have differing heat transfer fluids (HTF) and storage media. For those systems, the molten salt storage media (about 35 % of the direct capital costs) and the storage tanks (about 24 % of the direct capital costs) are the main bearers of cost. For direct systems with operating temperatures up to 560 °C, using molten salt as the HTF and the storage media, the capital cost ratios are 34 % for the storage media and 31 % for the storage tank, respectively[3]. In this context, three alternative concepts are presented in the following chapter.

(2) Literature review and selection of TES concept

In order to reduce the main cost bearers it is a straight forward idea to contain the storage medium molten salt in one single tank. Therefore two molten salt volumes at different temperature levels are stored in one container. Hereby, the main challenge is the minimization of the heat flux between the hot and cold volumes.

Single tank with floating barrier

The Spanish company SENER has developed a single tank storage system that divides and insulates the two volumes of hot and cold salt with a floating, barrier [4]. This approach was published by Copeland in a US Patent [5]. Figure 1 illustrates the main principle of this

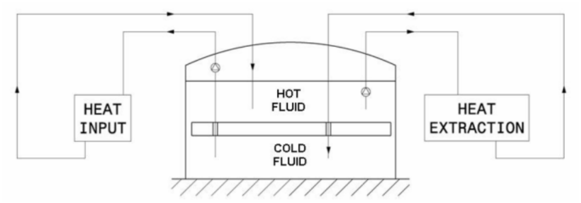

Figure 1 Principle scheme of a single tank storage with floating barrier [4]

concept. As shown in the scheme, a vertically guided floating disc is positioned between the hot and the cold salt volumes. Therefore the temperature dependency of the salt density is exploited. The barrier is designed to have a density value between those of the hot and the cold salt. Thus, the barrier floats upwards and downwards during the charging and discharging process. Querol et al. describes the following potentials for cost savings in comparison to a commercial two-tank system: 1) Avoidance of a second tank (unused containment volume), thereby 2) reduction of thermal losses and 3) special extended shaft pumps can be replaced by short shaft pumps. No numbers in terms of cost savings are given for this concept. Next step is the demonstration in an appropriate scale. SENER reported the completion of a pilot module in 2012 [6]. No final results could be identified in the literature since then.

Single tank with embedded heat exchanger

Another approach has been investigated by ENEA in Italy where one storage tank is necessary as well. The separation of the salt volumes in different layers is maintained by the different densities of the hot and cold salt volumes while the layers are in direct contact. Furthermore, the heat exchanger for the steam generation of the attached solar thermal power plant is embedded in the same containment as shown in Figure 2. During this process steam is generated and superheated on the tube side whereas the salt on the shell side cools down. Because of the increasing density, the salt is forced downwards and a natural circulation is induced. Gaggioli et al. published results of a demonstration storage system which approve the functionality of this approach [7].

Compared to a demonstration facility with a two tank storage and a capacity of 80 MWh_{th}, ENEA has calculated possible capital cost savings of 39 % for the combination of storage and steam generation [8]. Further research in a larger scale has to be done to prove the feasibility on a commercially relevant scale.

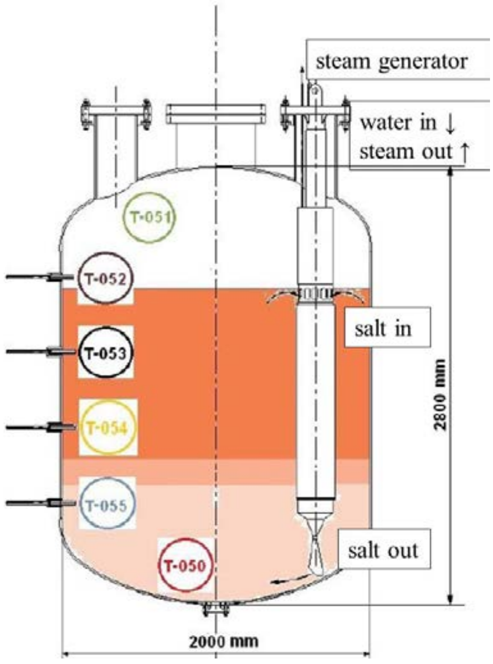

Figure 2 Principle scheme of a single tank storage with embedded heat exchanger [8]

Single tank with filler material

A widely known concept, developed by Sandia National Laboratories, is the thermocline-filler storage (TFS). Here, too, the separation of the salt volumes in different layers is maintained by the different densities of both volumes. In addition to this stratification, a packed bed of inexpensive solid filler material replaces about 50 – 75 % of the molten salt. Sandia build and tested a prototype with a storage capacity of 688 MWh_{th}, published in 2002 [9]. The tests were carried out with a maximum temperature of 400 °C. In charging mode, hot salt is pumped into the storage tank from the top and cold salt is taken from the bottom. While flowing through the packed bed, the thermal energy transfers between the molten salt to the solid filler material. During this process, a heat front moves through the packed bed from the top to the bottom as shown in Figure 3. The discharging mode works vice versa.

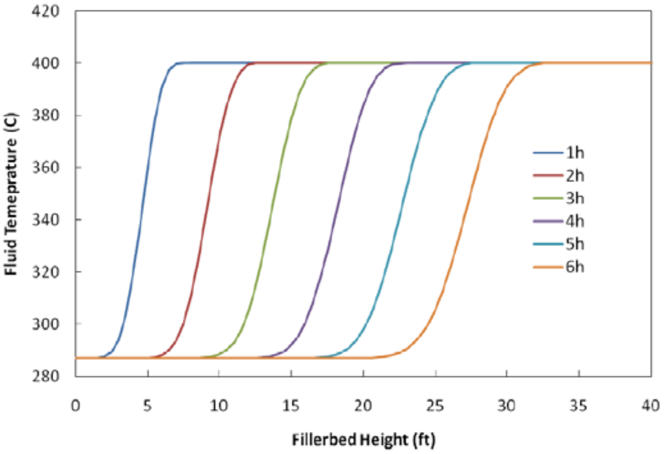

Figure 3 Simulated fluid temperature distribution in a TFS over the fillerbed height. The colored lines represent the distribution for different time steps. [10]

The cost reduction potential is estimated by Sandia to be about 20 % to 37 % [9]-[10] depending on storage size, direct or indirect storage and solar thermal power plant technology. Although extensive theoretical research has been carried out for the TFS concept in the recent years, for example by Flueckiger et al. [11], [12] or Li et al. [13], there are still several open questions and steps to take in order to make TFS commercially available.

DLR is working at the further development of the TFS at temperatures up to 560 °C. The following list highlights a selection of the important questions that have to be tackled.

- *Research of the filler material: material properties, alternative materials, durability*
  Sandia did extensive research on possible filler materials [14] available in the United States. However, there are natural materials in other parts of the world that are suitable for thermal storage applications. The characterization of these material candidates is incomplete in terms of thermodynamic properties, chemical stability in molten salt and their mechanical properties in packed bed applications.
- *Optimization of filler material parameters: e.g., porosity, particle size and distribution.*
  Depending on the composition of the packed bed, pressure losses, heat transfer and storage capacity and therefore the performance of the storage module varies.

- *Validation of thermo-mechanical and thermodynamic models*
  Tests on a representative scale are necessary to validate results that were derived from simulations.
- *Prototype operation experience for temperatures up to 560 °C*
  Operation and control modes for TFS concept in systems, e.g., start up or part load. No operational experience above 400 °C available.
- *Investigation of thermal ratcheting and possible reinforcements*
  This effect might occur when a packed bed has a considerably different thermal expansion than the steel from the container. During an operation with thermal cycling, stresses can possibly build up and result in container failure [11], [15].
- *Research and qualification for components operating at temperatures up to 560 °C*
  With a better understanding of the process technology of molten salt systems and further development for different components and instruments cost reduction can be achieved.

(3) Methodology

DLR performs various research activities to develop the TFS concept. Hence, the planning and erection of a large molten salt test facility are in progress as well as filler material investigations in the lab.

a) New test facility for thermal energy storage in molten salts (TESIS)

A new molten salt test facility called 'TESIS' is under construction at the DLR sight in Cologne. Start of operation is planned in the beginning of 2017. The facility has two main tasks, the development of alternative molten salt storage concepts and the investigation and qualification of molten salt components and instruments. Because of the different requirements the test facility is sub-divided into two independent sub-facilities, the *storage test facility* and the *component test facility*.

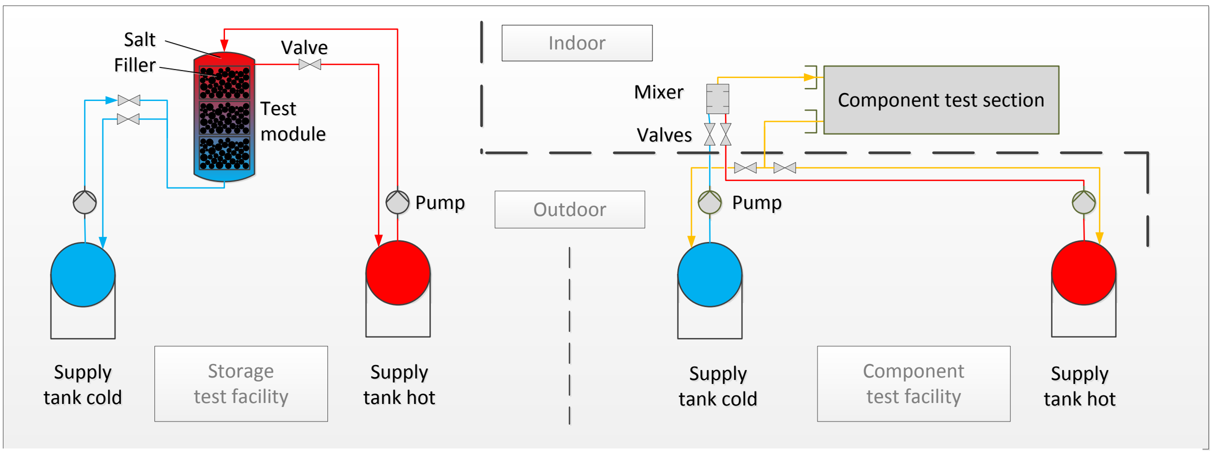

Figure 4 Simplified scheme of the TESIS sub-facilities (storage left, component right)

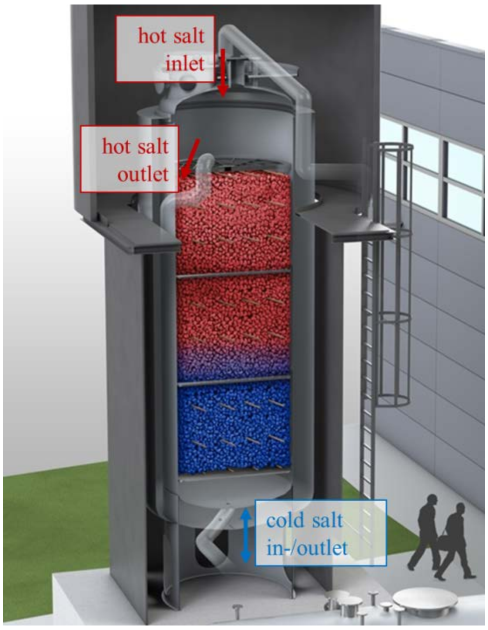

Figure 5 Model of the TESIS TFS test module. The test storage module contains a packed bed with several layers of thermocouples

Storage test facility

Figure 5 shows the set-up of the storage test facility. The tank for the storage tests can be opened at the upper boiler dish which is designed as a closure head. With this design it is possible to implement various test arrangements in the tank. To validate simulation results, several layers of thermocouples will be placed in the packed bed to measure the temperature distribution in a sufficient resolution. The tests on this facility will start with the TFS storage concept. For this purpose, the packed bed of filler material will be placed in three additional containers that are stacked in the tank. With this approach, different materials, different packed bed arrangements and different measurement arrangements can be researched.

In order to charge and discharge the storage, the tank is connected to two supply tanks which have different temperature levels. These supply tanks serve only for tests. In a real system these supply tanks are not necessary. Depending on the test requirements the temperature levels can be chosen freely within the design temperature listed in Table 1.

Figure 4 shows how the storage cycles are applied to the storage tank.

For the discharging process colder salt is pumped from the blue tank following the blue line to the bottom of the storage tank. The same amount of salt is returned through a level drain following the red tube red line. For the charging process hot molten salt is pumped from the red tank following the red line to the top of the storage tank while salt is withdrawn from the bottom of the storage tank and returned to the blue tank following the blue line. With this set-up, constant test conditions can be realized. The supply tanks are equipped with a cooler (blue tank) and an electric heater (red tank) to

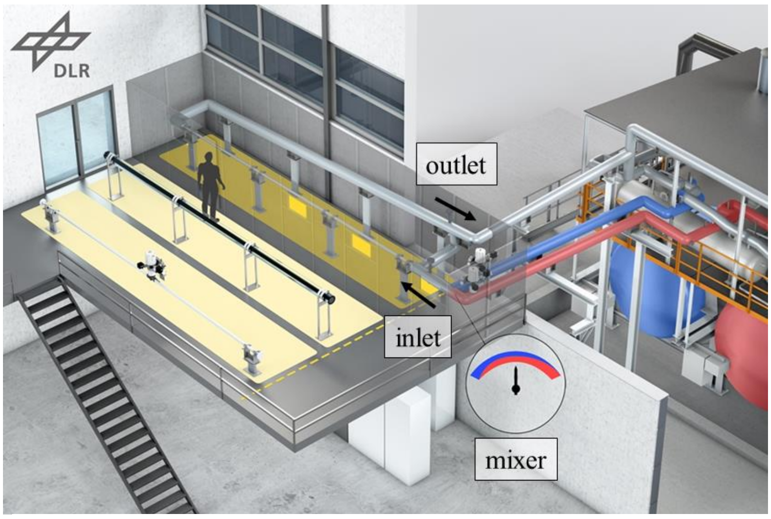

Figure 6 Model of the TESIS component test facility

Table 1 Summary of the TESIS test facility characteristics.

Sub-facility	Storage test facility	Component test facility
molten salt medium	Nitrate-Nitrite salt mixtures	Nitrate-Nitrite salt mixtures
min. operation temperature	150 °C	150 °C
max. operation temperature	560 °C	560 °C
max. mass flow rate	4 kg/s	8 kg/s
max. mass of filler material	45 t	n/a
max. salt storage volume (without filler material)	22 m³	n/a
max. thermal gradient at the test section inlet	n/a	50 K/s
max. heating power	n/a	420 kW
max. cooling power	n/a	420 kW

keep the salt inventory at a constant temperature level also with changing return temperatures.

Component test facility

Figure 6 shows the component test facility of the molten salt test facility. The actual test section is the enclosed yellow marked area. This part of the facility is flexible for adjustments or reconstruction for the needs of various components and instruments e.g. receiver tubes or valves, marked with a light yellow area. The test section is designed for tests that can result in failure within the enclosure. This allows the components to be exposed to their design limits. For this purpose molten salt at different temperature levels can be mixed before entering the test object. The following test conditions are possible:

- Isothermal tests
- Cycling tests
- Slow thermal gradients
- Sudden temperature changes

b) Compatibility of filler materials and molten salts

For a successful commercialization of a single storage with filler material, it is mandatory to prove the durability of the filler material. Due to their cost reduction potential, natural stones are considered as a promising filler material.

In the process of finding suitable natural stones, a screening with focus on material properties can be a first step. Gross density, specific heat capacity, thermal conductivity, material strength are relevant in this context. Furthermore material availability is a possible limiting factor for a commercial storage concept.

Generally, natural stones can be classified in magmatic, sedimentary and metamorphic stones. Stones with high gross density and high compressive strength can be found in all three groups. The properties of metamorphic stones depend strongly on the conditions during the formation process. Thus, generally valid statements are difficult. In the group of sedimentary stones quartzite and graywacke are potential filler materials. However, stones in this group often contain calcite [16] which is detrimental to its structural stability, due to possible decomposition at high temperatures. Magmatic stones are well suitable with regard to their mechanical properties as they tend to have high gross densities, high comprehensive strength and wear-resistance. With regard to thermal stability and compatibility with nitrate salt, a study on granite and taconite (magmatic and sedimentary, respectively) was published by [17]. In these tests both natural stones were exposed to a binary mixture of 46 wt.-% sodium nitrate and 54 wt.-% potassium nitrate. In the analysis granite showed erosion and dissolution processes and was therefore dismissed as a potential filler material. However, taconite showed no detrimental behavior. Taconite was also part of a more extensive study carried out by Sandia. In a process of thermal tests without salt as well as isothermal and cyclic tests with molten salt, quartzite, silica sand and taconite were identified as suitable filler materials. Quartzite and silica sand were selected for further research due to their availability and low costs. In these investigations formations on the quartzite surface as well as in pores and subsurface cracks were detected, which had no critical impact on the tested samples [9], [14]. The tests were designed to simulate a 30-year plant life by accelerated thermal cycles. Brosseau et al. points out that, if all time-related processes were captured adequately, no long-term ill effects would be expected.

Current research at DLR focuses on the replication and verification of the results derived by Sandia, with testing under different conditions in terms of stone origin, temperature level and salt type. In addition, the natural stones basalt and diabas have been examined as potential filler materials (Figure 7). Research on material properties is also part of the DLR studies but will not be part of this publication. First results are published in [18].

Material tests

The test plan for the natural stones includes the following steps:

- Calcite content. Reaction test with 10 % hydrochloric acid
- Thermal stability without salt contact. (thermogravimetric analysis from 40 °C to

Figure 7 Selected natural stones (left: quartzite, middle: basalt, right: diabas)

900 °C; heating rate 10 K/min

- Isothermal tests in salt, $NaNO_3$-KNO_3 (500 h, 1000 h, 5000 h, 10,000 h)
  Analysis concerning weight losses, visible changes, elemental composition analysis of the stone (quantitative evaluation of minerals by scanning electron microscopy)
- Cyclic thermal test in salt (100 cycles, 7 h each)
  Analysis concerning weight losses, visible changes, elemental composition analysis of the stone (quantitative evaluation of minerals by scanning electron microscopy)

For the thermal tests, aluminum oxide crucibles were loaded with the natural stones (30 g-60 g) and salt (around 50 g) and placed in chamber furnaces.

(4) Results/Discussion

In this chapter a summary of the results of 500 h and 1000 h tests on this topic are presented. More detailed descriptions are published in [18] and will be released in other publications.

Calcite content (before thermal tests)

Quartzite and basalt showed no indication of calcite content in untreated condition. However, calcite content was detected for diabas.

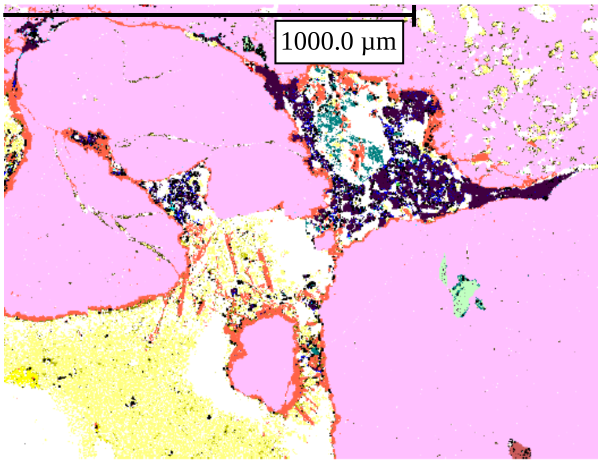

Figure 8 Quantitive analysis of minerals in quartzite after 1000 h exposure to $NaNO_3$-KNO_3 at 560 °C

Thermal stability without salt contact

The thermogravimetric analysis confirmed the test on the calcite content. For quartzite and basalt no progressive mass losses were measured. Diabas on the other hand experienced mass losses of 9 wt.-% in the first heating cycle and progressive mass losses in the following. Hence, diabas is dismissed for further investigations.

Isothermal tests in salt

Visible changes of color were detected for quartzite which changed from grey to rose. Additionally small cracks occurred on the surface. Basalt did not show visible changes.

The analysis of the mineral content (isothermal tests with 1000 h and cyclic thermal test with 100 cycles) that was carried out by an external research institute revealed a change of the material composition for both quartzite and basalt. It is expected that quartzite reacts with both components of the salt mixture:

Quartzite + $NaNO_3$ → Natrosilit ($Na_2Si_2O_5$) at the grain boundaries (red areas in Figure 8)

Quartzite + KNO_3 → KSiO phase; entering the pore and crack volumes (dark blue areas in Figure 8)

For basalt the detected changes are not yet fully understood. However, conversion processes occur in the grains at different stages. Both materials are under ongoing examination in order to completely understand the changes that occur and their impact on the durability of the natural stones.

Cyclic thermal tests in salt

In the current stage, no distinctive differences can be derived from the cyclic thermal tests in comparison to the isothermal tests.

The results show that longer tests are necessary to assess the composition changes in the filler material and the salt mixture. Thus, samples with Quartzite and Basalt from 5000 h tests are currently analyzed and 10,000 h tests are almost completed.

(5) Summary and conclusion

The current development on molten salt storage systems focuses on cost reduction. Within this context three developments of the recent years, are presented in this paper. Due to the need for further operational experience and several open questions on temperatures above 400 °C, DLR focuses its research on the thermocline filler storage (TFS) approach.

In order to answer some of the listed questions, DLR is currently setting up a test facility for molten salt storage and component tests. Construction works are in progress and start of operation is scheduled for spring 2017. Additionally, research has been done on a better understanding of the compatibility of potential filler materials for TFS. During 500 h and 1000 h tests quartzite and basalt remained stable but also showed some mineralogical changes. Samples of 5000 h and 10,000 h tests are currently under investigation to retrieve a better understanding of those changes and their consequences.

It can be concluded that, according to literature [3], [9], TFS offers significant cost reduction potential but still requires further research in the area of material, storage components and system integration for full commercial applicability.

(6) Acknowledgements

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