

## **ADVANCED HIGH TEMPERATURE LATENT HEAT STORAGE SYSTEM – DESIGN AND TEST RESULTS**

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### **ABSTRACT**

Processes with a two-phase heat transfer fluid (e.g. water/steam) require isothermal energy storage. Latent heat storage systems are an option to fulfil this demand. For high temperature applications nitrate salts are suitable materials for phase change storage. The main drawback of these materials is the low thermal conductivity, limiting the power density during the charging/discharging process. At DLR the so called sandwich-concept has been developed to realize latent heat storage with high power densities for applications in solar thermal power plants and process industry. This concept has already been demonstrated successfully for three different storage units ranging from 2-100 kW at melting temperatures of 142 °C and 222 °C. In 2008, a test storage using sodium nitrate as phase change material (PCM) with a melting temperature of 306 °C was operated in a 5 kW laboratory loop. The designed heat transfer rate was achieved and after 172 cycles no degradation was observed.

### **1. INTRODUCTION**

The demand for storage systems operated by condensating/evaporating steam is increasing due to the successful demonstration of direct steam generation in parabolic troughs [1], the start of operation of the PS10 solar tower plant producing saturated steam and projects aiming at the generation of solar process steam.

In a direct steam generation plant the pinch point topic for the water/steam cycle makes it unattractive to use only sensible heat storage. There, a three component storage system combining sensible and latent heat storage is advantageous. The heat needed for evaporating the water is stored in the latent heat storage, while the heat for preheating and superheating is stored in sensible concrete storage units. This technology is currently being developed by DLR, Ed. Züblin AG and Siemens AG within the project ITES, funded partly by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety.

Latent heat storage relies on phase change materials (PCM) that can undergo phase transitions, e.g. from a solid to a liquid state. This permits the storage of large amounts of heat within a narrow temperature interval. The current status of latent heat energy storage systems for steam results mainly from recent research projects at DLR aiming at the development of cost effective concepts intended for process heat applications with a pressure between 1 and 40 bar and for power generation with a pressure range of 20 to 130 bar. The selection of the suitable phase change material and the design of the heat transfer concept between storage material and steam represent two essential tasks in the development of latent heat storage systems.

## 2. PHASE CHANGE MATERIAL

The selection of phase change materials depends on the parameters of the steam process. For process heat applications the required phase change temperatures of suitable storage materials lie in the range of 100 °C to 250 °C and for solar thermal power generation between 210 °C and 330 °C depending on the saturation temperature of the steam process.

While a lot of materials show melting temperatures in these temperature ranges, the number of materials regarded as promising options for cost effective latent heat energy storage is limited. Low melting metals (tin, lead) and lithium nitrate ( $\text{LiNO}_3$ ) must be excluded due to cost aspects; chlorides corrode steel and show a high hygroscopicity. Among other alkali metal nitrates and nitrites, potassium and sodium nitrate and binary mixtures of the two are very suitable, covering the temperature range of 140 °C - 330 °C. Figure 1 shows the melting enthalpy and the melting point for selected mixtures of alkali nitrates and nitrites [2].

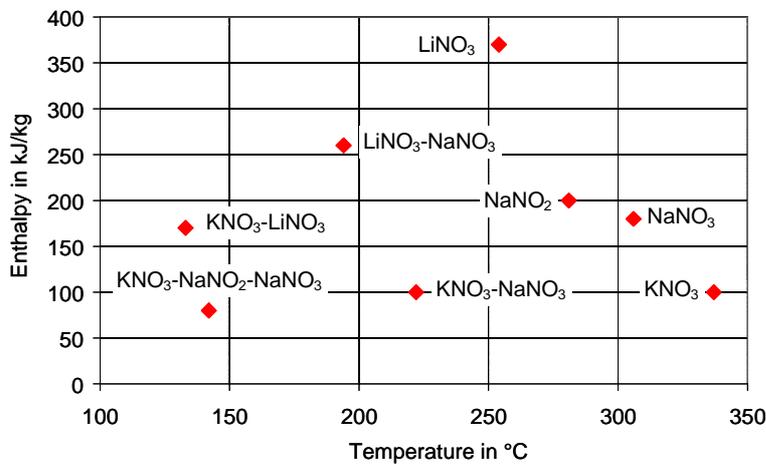


Figure 1: Selected alkali nitrates / nitrites as PCM storage materials

Lab-scale operation of the three materials given in Table 1 has already been proven in different test modules at DLR. The estimated costs are only considering rough costs of the storage material divided by its latent heat to give an indication on the suitability of the storage material itself. The costs of the heat exchanger and of the heat transfer enhancement structure, which are a major portion of storage costs, are not included here.

	Melting temperature in °C	Heat of fusion in kJ/kg	Density (liquid) in kg/m <sup>3</sup>	Capacity Latent heat in kWh/m <sup>3</sup>	Estimated costs in \$/kWh only material, only latent heat
$\text{KNO}_3\text{-NaNO}_2\text{-NaNO}_3(\text{eu})$	142	60	1980	33	52.5
$\text{KNO}_3\text{-NaNO}_3(\text{eu})$	222	100	1960	54	17.5
$\text{NaNO}_3$	306	175	1910	93	9.5

Table 1: Candidate materials for latent heat storage systems

Results of detailed material investigations of  $\text{NaNO}_3$  are presented in a paper by Bauer et al. at this conference.

### 3. ENHANCEMENT OF HEAT TRANSFER RATES OF LATENT HEAT STORAGE

Since the working fluid is not used for energy storage, an indirect heat exchanger concept for the exchange of thermal energy between working fluid (usually pressurized water/steam) and the phase change storage material is needed. The biggest technological problem for the implementation of high-temperature latent heat storage systems is the insufficient thermal conductivity of the available phase change materials. Most salts provide a thermal conductivity around  $0.5 \text{ W}/(\text{m}\cdot\text{K})$ .

During the discharge process, the energy released by solidification of the storage material must be transported from the solid-liquid interface through the growing solid layer to the heat exchanger surface (Figure 2). Therefore the heat transfer coefficient is dominated by the thermal conductivity of the solid PCM. So the main task in the heat exchanger design process is to identify cost effective options to increase the effective heat conductivity within the storage material.

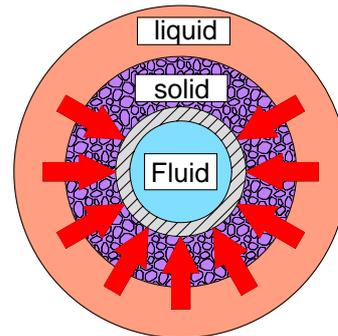


Figure 2: Solification of PCM around heat exchanger tube during discharging

Different options have been investigated to overcome the limitation resulting from the low thermal conductivity of the storage material [3]. The sandwich concept has been identified as the most promising option to realize cost-effective latent heat storage systems. Here, fins enhance the heat transfer within the storage material. The heat transfer area is increased by mounting the fins vertically to the axis of the tubes. The characteristic height of these fins exceeds the dimensions which are commercially available as finned tubes. Decisive for the successful implementation of this approach is the selection of the fin material. Table 2 shows relevant properties for various materials.

	Graphite foil	Aluminum	Stainless steel	Carbon steel
Thermal conductivity in $\text{W}/(\text{m}\cdot\text{K})$	150	200	20	30
Density in $\text{kg}/\text{m}^3$	1000	2700	7800	7800
Volume spec. costs (estimated) in $\$/\text{m}^3$	10000	7000	20000	15000

Table 2: Materials considered for fins

Steel fins seem to be a straightforward solution, since they are clearly compatible to the steel tubes. Instead, graphite foil or aluminum is chosen as fin material due to their favorable heat conductivity. As shown in Figure 3, steel fins showing the same heat transport performance as fins made of graphite foil demand much more volume. Therefore the costs for steel fins are significantly higher, also due to the higher density.

The application of fins made of expanded graphite offers several advantages besides good thermal conductivity. Expanded graphite shows good chemical stability in nitrates and nitrites at temperatures up to  $250 \text{ }^\circ\text{C}$  and galvanic corrosion does not occur in contact with steel tubes. Since graphite foils, often used as sealing material, show a high flexibility, a close contact between tubes and fins can easily be realized.

Aluminum fins are applicable for temperatures up to 330 °C. The mounting of the fins on the tubes is an essential issue for the sandwich concept. Galvanic corrosion of aluminum with carbon steel and sodium nitrate has been analyzed, showing no critical corrosion. A good mechanical contact between fins and tubes is important.

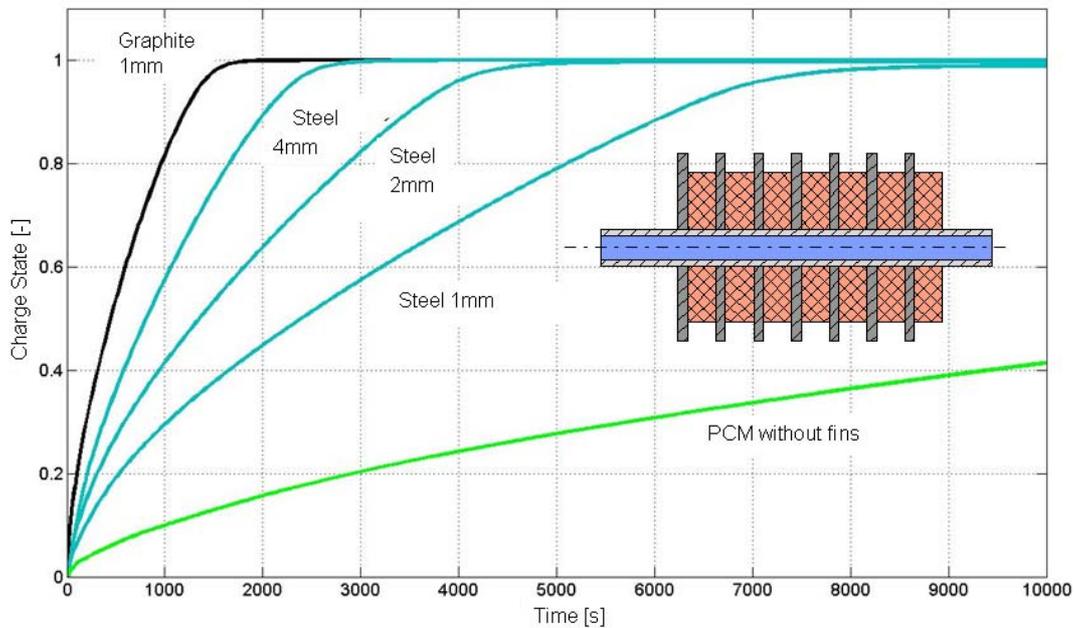


Figure 3: Comparison of charge state for PCM without fins, with steel fins of different thickness and with graphite fins

#### 4. EXPERIMENTAL DEMONSTRATION

In the initial phase of the development of PCM storage systems based on the sandwich concept, three test units with varying power and capacity have been designed, manufactured and tested, using graphite foil as fin material. Table 3 lists characteristic parameters of these test units, which demonstrated the feasibility of the sandwich concept and the durability of graphite fins.

Identification	Max. power in kW	Capacity in kWh	PCM	PCM mass in kg	Melting temperature in °C	Working fluid
DISTOR I	2	3.5	KNO <sub>3</sub> -NaNO <sub>3</sub> (eu)	130	222	Thermal oil
PROSPER	15	7	KNO <sub>3</sub> -NaNO <sub>2</sub> -NaNO <sub>3</sub> (eu)	400	142	Steam provided by test facility
DISTOR II	100	55	KNO <sub>3</sub> -NaNO <sub>3</sub> (eu)	2000	222	Steam provided by parabolic troughs

Table 3: Test storage units using graphite fins

The test units showed very high specific discharge powers. The experiments did not show any degradation of the graphite foils or the PCM resulting from the charging/discharging cycles. Based on the results gained during the manufacturing and operation of these prototypes, the current development focuses on the thermo-economic optimization of the graphite-based sandwich concept. The geometry of the finned heat exchanger shows potential for improvements by modification of the shape of the fins; also optimization of the production processes will further reduce the capacity-specific costs.

In 2008 at DLR, a first PCM storage module using sodium nitrate ( $\text{NaNO}_3$ ) was tested successfully in the kW-range. The storage module is filled with approx. 140 kg of sodium nitrate with a melting temperature of  $306\text{ }^\circ\text{C}$ , a heat of fusion of  $175\text{ kJ/kg}$  and specific heat capacities of  $1.5\text{ kJ/(kg}\cdot\text{K)}$  in solid and  $1.7\text{ kJ/(kg}\cdot\text{K)}$  in liquid state around the melting temperature. In this temperature range graphite and  $\text{NaNO}_3$  are not compatible, therefore aluminum fins are applied. The PCM test module has an external diameter of  $30.8\text{ cm}$  and a height (without pedestal) of  $1.4\text{ m}$  (Figure 4). It comprises seven heat exchanger tubes equipped with aluminum fins (Figure 5).

If a PCM storage containing  $\text{NaNO}_3$  is to be operated with water/steam as heat carrier fluid, assuming a driving temperature difference of  $10\text{ K}$  between steam cycle and storage system, the steam has to condensate at  $316\text{ }^\circ\text{C}$  while charging and water has to evaporate at  $296\text{ }^\circ\text{C}$  during discharge. By the vapor pressure curve, the saturation temperature is directly linked to an operating pressure of  $107\text{ bar}$  at  $316\text{ }^\circ\text{C}$  and  $81\text{ bar}$  at  $296\text{ }^\circ\text{C}$ . Such demanding steam parameters are difficult to realize in laboratory scale, therefore a test facility using the thermal oil Therminol VP-1 as heat transfer fluid was employed.

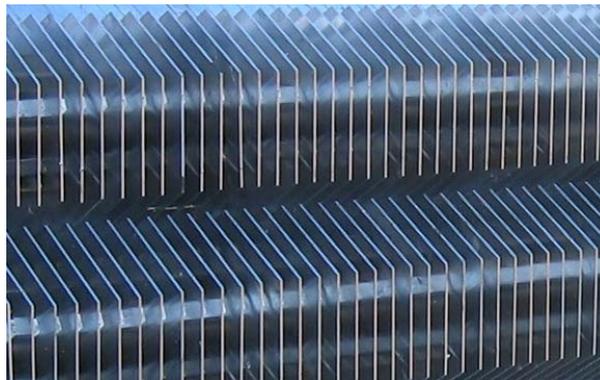


Figure 4:  $\text{NaNO}_3$  PCM Storage Test Module

Figure 5: Fins for heat transfer enhancement

To calculate the theoretical capacity of the test module, the mass of all integrated materials (containment, heat exchanger tubes, fins, end-plates, thermal oil and phase change material) has been determined and the thermal capacity has been calculated from the single masses times their specific heat capacities. This results in a total thermal capacity of  $0.30\text{ MJ/K}$  for temperatures below the melting point of  $306\text{ }^\circ\text{C}$  and  $0.33\text{ MJ/K}$  for temperatures above the melting point. The latent heat during phase transition at  $306\text{ }^\circ\text{C}$  is  $24.41\text{ MJ}$ . So for a temperature difference of  $20\text{ K}$  ( $296\text{ }^\circ\text{C} - 316\text{ }^\circ\text{C}$ )  $30.63\text{ MJ}$  ( $8.51\text{ kWh}$ ) can be stored. The relevant volume of the test module is  $0.102\text{ m}^3$ ; it was calculated by deducing the volume of a head space that was unintentionally not filled from the "outer volume" of the module including the pipes to the flanges but not the pedestal. So the theoretical specific storage capacity is  $83.3\text{ kWh/m}^3$ . In a full scale module the

ratio of the mass of the steel containment to the PCM mass is more favorable than in the lab scale module, the specific storage capacity is expected to increase for larger modules.

In Figure 6, a typical cycle from an experiment with a flow of  $3.9 \text{ m}^3/\text{h}$ , with 3.5 hours charging time and 2.5 hours discharging time is plotted, showing clearly the isothermal segments for the PCM at  $306 \text{ }^\circ\text{C}$ . Due to the limited heating power of the test facility, the oil inlet temperature during charging can not be applied as a step function. The available cooling power is much higher, therefore here a step function can be approximated and the breakpoint during discharging it is only about 1 hour, while for charging it is about 1.8 hours.

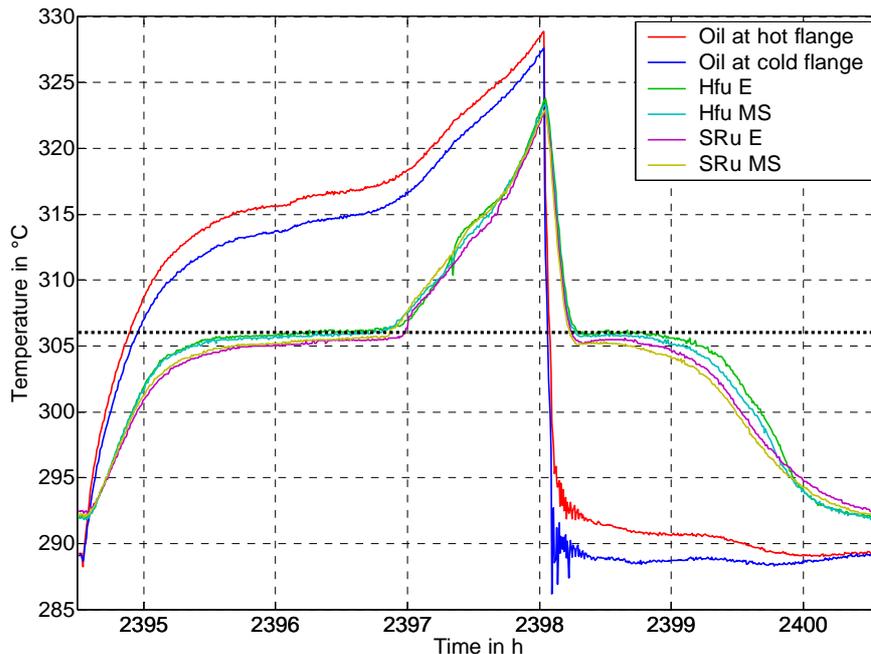


Figure 6: Experimental results of a typical charge and discharge cycle

The measured data of the automatic cycling program shown in Figure 7 has been analyzed to determine the specific storage capacity and power of the test module. The vertical lines mark the limits for integration (orange for charging, cyan for discharging). These were drawn at  $296 \text{ }^\circ\text{C}$  and  $316 \text{ }^\circ\text{C}$  mean temperature of the PCM at the 9 thermocouples in the bottom of the storage unit, so that the time span for integration comprises a temperature difference of  $20 \text{ K}$ . The heat loss to the environment as a function of the containment wall temperature had been determined in steady state experiments at various temperature levels. At the melting temperature of  $306 \text{ }^\circ\text{C}$ , the heat loss was about  $430 \text{ W}$ . In the charge processes shown in Figure 7,  $7.87 \pm 0.03 \text{ kWh}$  were stored into the module and during the discharge processes  $7.20 \pm 0.05 \text{ kWh}$  were released. This corresponds to a mean power of  $2.9 \text{ kW}$  and  $4.3 \text{ kW}$  respectively. The lower power during charging is due to the limited heating power of the oil circuit used. During discharge a mean specific power of  $42.5 \text{ kW/m}^3$  was reached. This result confirms the design data and proves the applicability for solar thermal power plants, where for typical storage capacities of around 6 hours, the required specific power lies in the range  $15\text{-}20 \text{ kW/m}^3$ .

The difference between the theoretical heat capacity of  $8.51 \text{ kWh}$  and the experimental results is explained mainly by uncertainties in the measurement of the oil temperature. According to EN 60 751, the limiting deviation  $\Delta T$  of PT100 sensors of class A is  $\pm(0.15 + 0.002 \cdot t)$ ,  $t$  being the temperature in  $^\circ\text{C}$ . Hence, for  $306 \text{ }^\circ\text{C}$  oil temperature the deviation can be up to  $0.8 \text{ }^\circ\text{C}$ . At a flow

of 3.9 m<sup>3</sup>/h, already a deviation of 0.11 °C in the temperature difference accumulates to 0.64 kWh in 165 min (the mean duration of the charging periods evaluated). So, within the experimental limitations, the test results and the expectations are in good agreement.

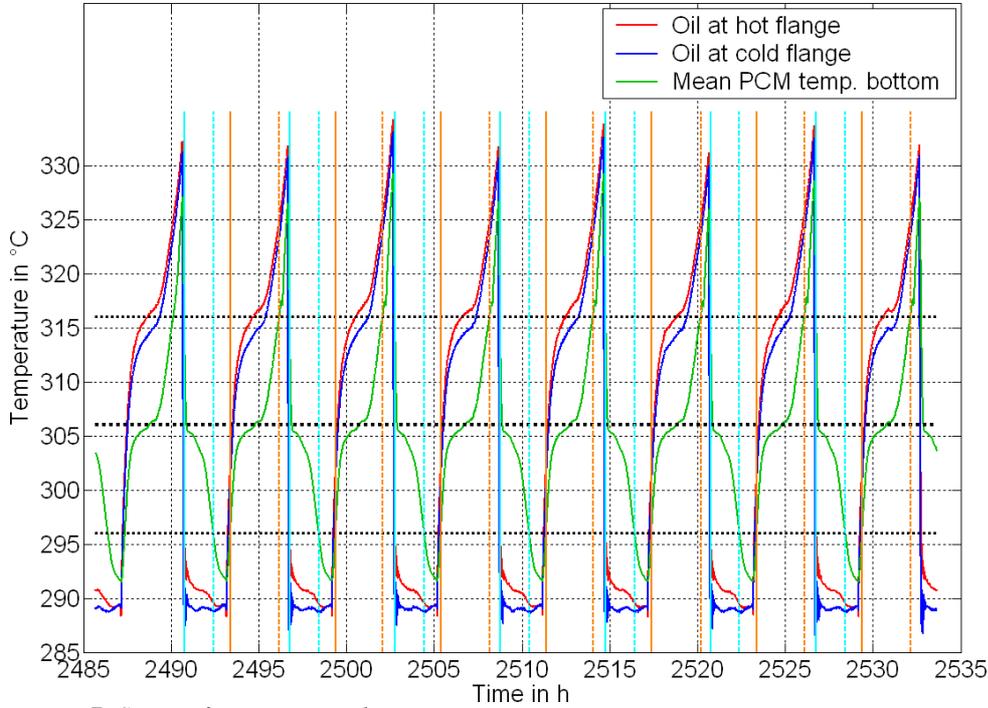


Figure 7: Series of automatic cycles

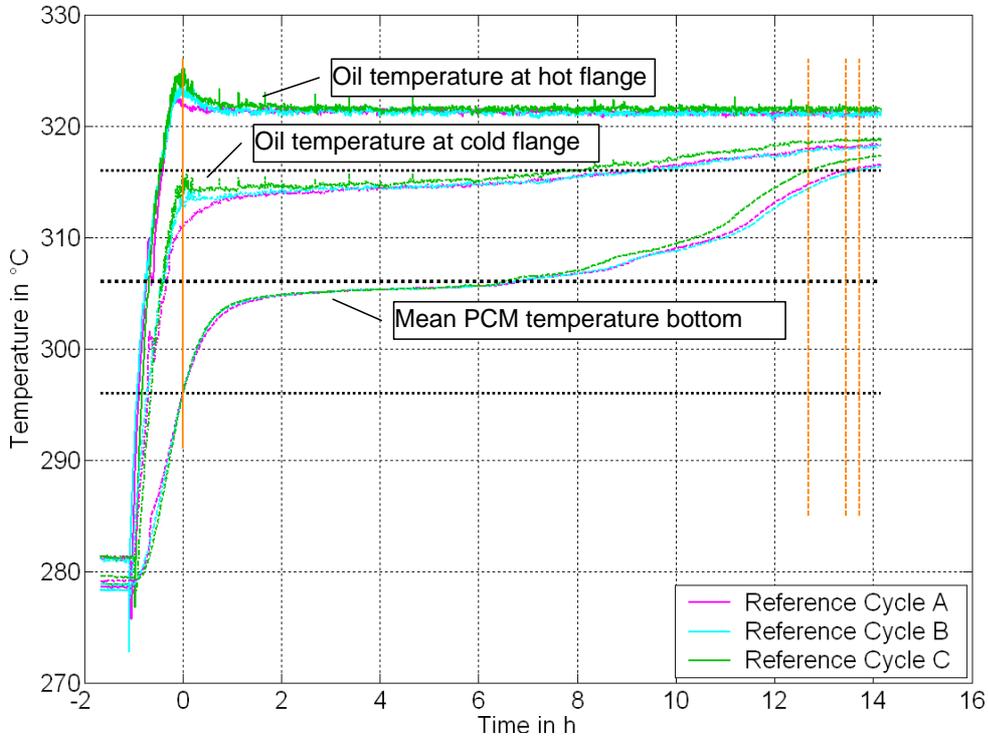


Figure 8: Superposition of reference cycles run 2927, 3574 and 3867 hours after start of operation

Overall, the storage test lasted more than 4000 h and comprised 172 cycles. During this test no change in the melting temperature of the salt was detected (Figure 8). Also the fins inside the storage showed no degradation at all. With this design configuration very high specific power levels were achieved, so it is proven that the major problem of PCM storage in the past [4] has been overcome and PCM storage with a large capacity factor is possible.

To demonstrate a combined storage system for direct steam generation, a storage system with a PCM module for evaporation of water and a concrete storage module for superheating of steam was designed and is currently being fabricated. The system has a total storage capacity of approx. 1 MWh and will be tested in 2009 in a test-loop with real-life steam parameters at the power plant Litoral of Endesa in Carboneras, Spain.

## 5. SUMMARY AND CONCLUSIONS

High temperature latent heat storage with high capacity factors was demonstrated at different temperature levels. The sandwich concept using fins made either from graphite or aluminum was proven as the best option to realize cost-effective latent heat energy storage. The application of graphite is preferred for applications up to 250 °C; at higher temperatures aluminum fins are used. Feasibility was proven by three prototypes using graphite and by a further storage unit using aluminum fins. A PCM storage with a capacity of approx. 700 kWh is currently being fabricated. Other activities aim at the thermo-economic optimization of the storage concept; further storage systems using the sandwich concept are under development.

## ACKNOWLEDGEMENTS

The authors would like to thank the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety for the financial support given to the ITES project (Contract No. 03UM0064).

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