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## Transfer of laboratory results on closed sorption thermo-chemical energy storage to a large-scale technical system

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### Abstract

The studies reported here are focused on the development of an efficient, closed thermo-chemical heat storage system in an appropriate scale for the integration into industrial processes as well as heating systems. Such a storage method offers several advantages including the possibility of long-term storage with minimal thermal losses and a high-energy storage density compared to sensible and latent thermal storage principles. This makes it possible for medium-temperature solar collectors and other heat sources of high potential to be applied in industrial processes; which is rarely done nowadays due to the lack of suitable thermal storages. From the results of the tests on a laboratory scale unit with 1.5-liter storage volume, suitable storage materials as well as optimal process conditions such as the temperature and pressure ranges were identified. Applying these attained process conditions, different heat exchanger concepts were developed, tested and optimized in 15-liters storage units. The result was a new heat exchanger configuration that showed a more than 60 % higher heat power rate than measured with standard heat exchangers in the bulk. The concept comprises a combination of several measures to increase the storage density by improving the mass and heat flow in the system with minimum loss of storage volume. As the last step, this improved concept was applied in an up-scaled heat storage system with 750-liters storage volume.

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*Keywords:* Adsorption; zeolites; composites; up-scaling; thermo-chemical; heat storage; heat exchanger; adsorptive

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### 1. Introduction

Thermal energy storage is necessary for an efficient use of solar heat and other heat sources for both domestic purposes and industrial processes. Furthermore, it improves the contribution of solar thermal systems to the overall energy supply significantly and plays an important role in balancing the energy's supply and demand. One method to store thermal energy is based on a sorption principle, where water,

evaporated at a low temperature level, is adsorbed on a highly porous material to discharge the system. Whereas, the charging mode is an endothermic process by which thermal energy is required to remove the weakly adsorbed water. During the storage period the two reaction partners, adsorptive and adsorbent, can be kept separately. Since, the energy is stored indirectly by means of physico-chemical processes, it can be stored even for a very long period without significant thermal losses. Therefore, this kind of system can be considered as a thermally driven heat pump with long cycle periods.

Sorption thermo-chemical heat storage has been a subject of several investigations during the last decade due to the important advantages it offers compared to sensible and latent thermal storage methods. The storage density can theoretically be several times higher than sensible storage in water; i.e. these systems can store much more energy without requiring a bigger construction volume. Depending on different parameters such as the working medium and the available energy source, the thermal storage through sorption thermo-chemical method can be done in a wide temperature ranges. However, most of the studies reported have focused mainly on thermo-analytical sorption material characterization or restricted on investigation on small-scale systems [1 - 4]. While some research and development activities have been executed in the past on an open system, the technology is still under development [5 - 6]. Thus, particularly more advanced sorption materials and system configurations on large scale systems are still needed for an efficient thermal storage at higher temperatures, especially in the range of 60 – 250 °C. This wide temperature range offers a high potential for medium-temperature solar collectors (Fresnel collectors, advanced evacuated tube collectors, etc.) to be applied in industrial processes, which is rarely done nowadays due to the lack of suitable heat storages [7].

The main objective of the studies presented here was to develop a closed sorption thermo-chemical heat storage system in a relevant scale for the integration in industrial processes and heating systems. One aspect of the studies reported focused on the experimental and theoretical characterization and modification of different sorption materials for wide temperature range application. While the other aspect focused mainly on system design and development in different sizes by up-scaling from lab scale with a storage volume of 1.5 to 15-liters and finally a large technical system of 750-liters storage volume.

## **2. Experimental part**

### *2.1. Experiments in lab-scaled test rig with storage volume of 1.5-liter*

The lab-scale experiments described here are generally divided into two parts that each has its own significance. While, the first part focused on a material characterization through determining specific adsorption behaviours of different sorption materials; the second part concentrated on system development and process characterization. The first step of the material characterization was screening a wide range of micro- and meso-porous sorption materials (pore size 0.3 - 50 nm) mainly using static adsorption under vacuum followed by dynamic desorption for pre-selection of suitable materials.

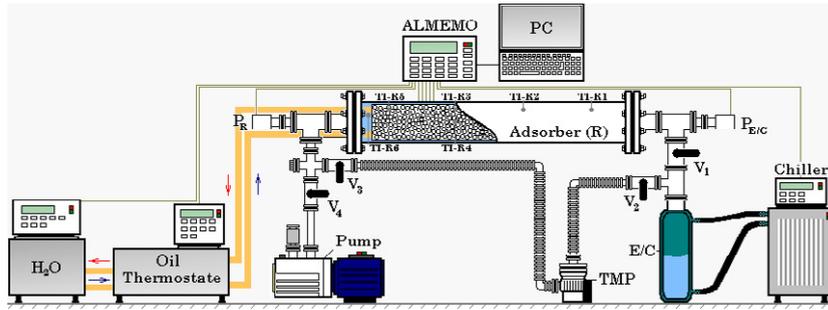


Fig. 1. Schematic diagram of the 1.5 L lab-scale storage test rig

Moreover, an extensive material as well as heat storage process characterization have been performed using some of the already selected sorption materials (800 – 900 g) in a lab-scaled test rig with storage volume of 1.5 L (Fig. 1) to measure different process and thermodynamic parameters such as temperature and pressure gradients, adsorption capacities, energy densities, kinetics, mass flow resistance, as well as short term hydrothermal stability under defined charging/discharging process conditions ( $T_{V/C} = 30\text{ }^{\circ}\text{C}/10\text{ }^{\circ}\text{C}$ ,  $p_{\text{H}_2\text{O}} = 42/12\text{ mbar}$ ). The maximum charging temperature ( $T_D$ ) ranges from 90 to 200  $^{\circ}\text{C}$  depending on the type of the investigated material. In all cases water has been selected as an adsorptive due to its higher vaporization enthalpy, dipole character, easily availability, a non-toxic character and lower price. These experiments were conducted using the same test rig as described in previous work with some modifications [3].

## 2.2. Experiments in lab-scaled advanced test rig with storage volume of 15-liters

Prior to building an efficient technical large-scale storage system a detailed knowledge on the behavior of the single components, particularly their interaction during charging and discharging was necessary. Therefore a further small but flexible lab-scale storage system with 15 L storage volume was build with the focus to investigate important process conditions and to test different heat exchanger concepts. The purpose of this was to increase heat storage density to a maximum of 220 kWh/m<sup>3</sup> and the heat power rating during charging/discharging through optimizing the overall heat conductivity of the storage material bulk as well as to develop the process technology including the controls. For this purpose different heat exchanger concepts were designed and tested. Furthermore, a number of process conditions were tested to enhance the understanding of the technology and to facilitate the upscale of the reactor. Figure 2a and 2b shows the 15 L lab-scaled test rig including the storage main subsystems and the placement of the thermo-couples within the storage module. The storage main subsystems are: 1) Storage reactor (R) where the reaction for charging (desorption phase) and discharging (adsorption phase) of the heat takes place. It further comprises of adsorbent, heat exchanger, gas flow channels, copper thin plates and six thermo-couples 2) Evaporater/Condenser (E/C), in which the working fluid is evaporated during adsorption and condensed during desorption 3) Water reservoir (WR) to adjust the water level in the E/C during the whole cycle 4) Oil thermostat (OT) that simulates a high temperature heat source 5) Vacuum pump to keep the system under vacuum conditions. 6) Thermo-couples, pressure sensors, capacitive water level control unit, measurement and control systems.

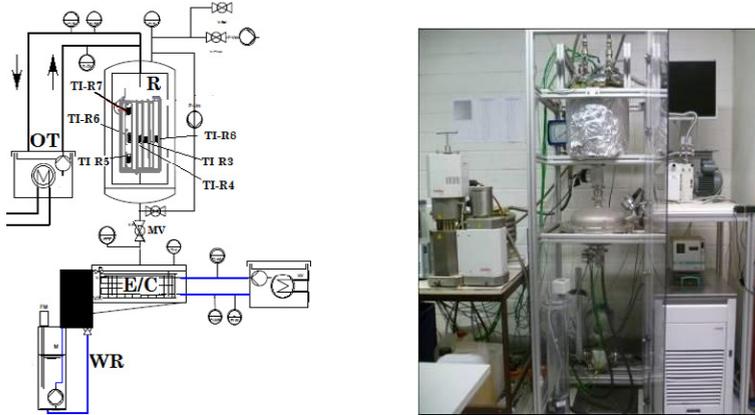


Fig. 2. (a) The schematic diagram of the 15 L lab-scale test rig; (b) The test rig

### 2.3. Development and test of up-scaled system with storage volume of 750-liters

Based on the research and technical experiences obtained from the 15 L test rig, the up-scaled heat storage system with 750 L storage volume (Fig. 3a) was built and tested. The main subsystems are identical to the advanced lab scale test rig. Several experiments were conducted under more realistic conditions in order to support the results from lab-scale experiments. The dynamical characteristics of the components and the whole storage system were investigated. Since the adsorbent used (ca. 510 kg) had been delivered with moisture content less than 1 %, activation of the system prior to adsorption was not necessary. Thus, the process began with discharging (adsorption) the system. Prior to the adsorption process, water is pumped from WR into the E/C. The water level in the E/C is kept constant to a level until the water surface reaches the upper end of the heat exchanger. The water cycle delivers the heat of evaporation to keep the temperature in the E/C constant at 20 - 30 °C. Once the water has reached the desired temperature, the main valve (MV) is opened. Due to the resulting pressure difference between E/C and R ( $p_R < p_{E/C}$ ), the water vapour flows into the storage reactor. In this way adsorption, exothermic interaction of the adsorbent and the adsorptive takes place. In this way, the binding and condensation energy is released in terms of thermal energy. This released energy is then withdrawn over the oil cycle through the heat exchanger inside the storage reactor. Because of the ongoing adsorption of the water vapour, a driving pressure difference between E/C and storage reactor keeps the process going. The reaction and the heat released decreases with an increasing loading of the adsorbent. The experiment is completed when the  $p_R$  and  $p_{E/C}$  are equal, suggesting that the adsorbent is completely saturated and equilibrium has been reached. Fig. 3b simulates the beginning and equilibrium state of the adsorption phase with respect to the pressure difference between the storage reactor ( $p_R$ ) and E/C ( $p_{E/C}$ ).

On the other hand, to charge (desorption) the system the thermo oil in the OT is heated to a maximum temperature of 200 °C and is pumped through the heat exchanger in the storage reactor. Thereby the sorption material is heated and due to the increase in temperature the water begins to desorb. On the other hand the temperature inside the E/C is kept to 15 - 20 °C. Due to the resulting pressure difference ( $p_R > p_{E/C}$ ), the desorbed water vapour starts to condense. The resulting heat of condensation is released to the consumer over the water recirculation heater/cooler. Once an equilibrium corresponding to the prevalent temperature and pressure is reached, the charging process is finished and the main valve (MV) is closed.

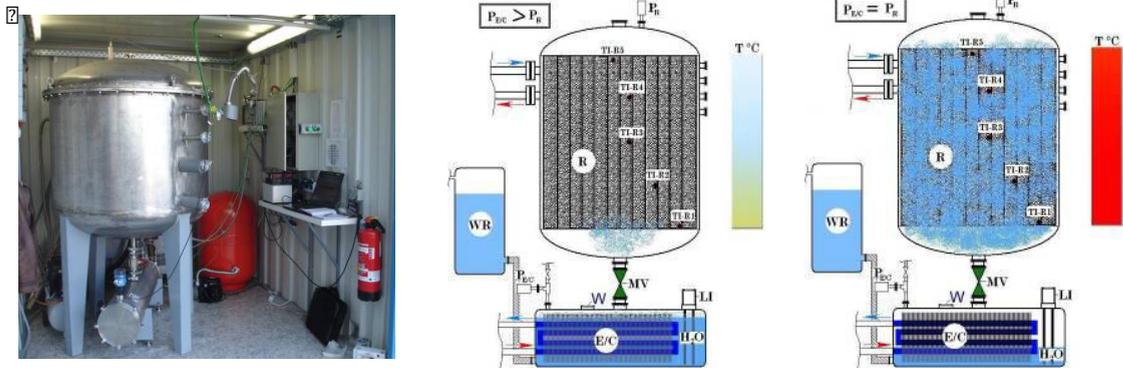


Fig.3. (a) Up-scaled system with a 750 L storage volume; (b) Simulation of the adsorption process based on the pressure difference (beginning  $p_R < p_{E/C}$ ; equilibrium  $p_R = p_{E/C}$ )

### 3. Results

Several results have been obtained from the experimental characterization tests that were performed mainly on two groups of sorption materials, namely on synthetic zeolites and composites (matrix of salt hydrates/porous material). Most of the zeolites used for these studies were obtained from CWK Bad Köstritz. Based on the results, presented here exemplarily in the form of water adsorption capacities, obtained from the static adsorption experiments that have been performed under different relative humidity ( $RH = 75 - 100 \%$ ), it was possible to make a pre-selection of suitable adsorbents for further detailed characterization. The equilibrium in most of the tests was reached within a week after the start of the adsorption. A series of dynamic tests were also performed to determine the adsorption behaviour including the mass transfer coefficients. Table 1 summarizes the results obtained from both static and dynamic studies carried out on different adsorbents. The static experimental results show that in most cases, more favourable adsorption capacities were achieved at higher relative humidity as expected. On the other hand, the unexpected higher results obtained from the composites Poolkohl and Attapulgit, with 30 % of  $CaCl_2$  content, in comparison to the previous reported results can be explained in terms of the formation of liquid water during adsorption due to the oversaturation of the materials at higher RH about 90 - 100% [3]. In the case of dynamic experiments, it has been found that the effect of the volumetric rate of the inlet moisture on the adsorption behaviour of the investigated sorption materials was insignificant. To validate the test procedures, some of the previously investigated materials have been also characterized in these studies. Some differences between the results from the previous studies on some of the materials, may be attributable to variability in experimental conditions and in particular that of temperature and pressure.

Table 1. Summary of the adsorption capacities obtained through static and dynamic tests

Sorption material	Bead size/Pellet $\varnothing$ [mm]	Bulk density [g/l]	Adsorption capacity (static) at RH = 75%/100% [g/g]	Adsorption capacity (dynamic) [g/g]
Zeolites				
NaMSX-CWK (I)	1.6 – 2.5	650	0.275/0.301	0.272
NaMSX-CWK (II)	2.5 – 3.5	670	0.282/0.286	0.268
NaMSX-CWK (III)	2.5 – 5.0	651	0.204/0.230	0.196
NaMSY	2.5 – 3.5	754	0.206/0.223	0.142
4ABF	1.5 – 2.5	612	0.248/0.252	0.242
4AK	1.5 – 2.5	688	0.218/0.232	0.206
Composites				
Poolkohl (pellet)	-	643	0.512/0.566	0.450
Attapulgit (pellet)	3.0 – 3.2	950	0.420/0.601	0.316

### 3.1. Experiments in lab-scaled test rig (1.5 L)

Fig. 4 shows the results obtained from adsorption experimental tests that have been carried out on some of the pre-selected micro- and mesoporous storage materials in the 1.5 L lab-scaled storage test rig. The displayed data include the measured thermodynamic parameters such as temperature and pressure, as well as parameters calculated from those measured thermodynamic parameters - energy, heat power and water loading during adsorption and desorption processes. At the beginning of the experiment during adsorption, equilibrium favours adsorption of the water vapours by the dry adsorbent that lead to

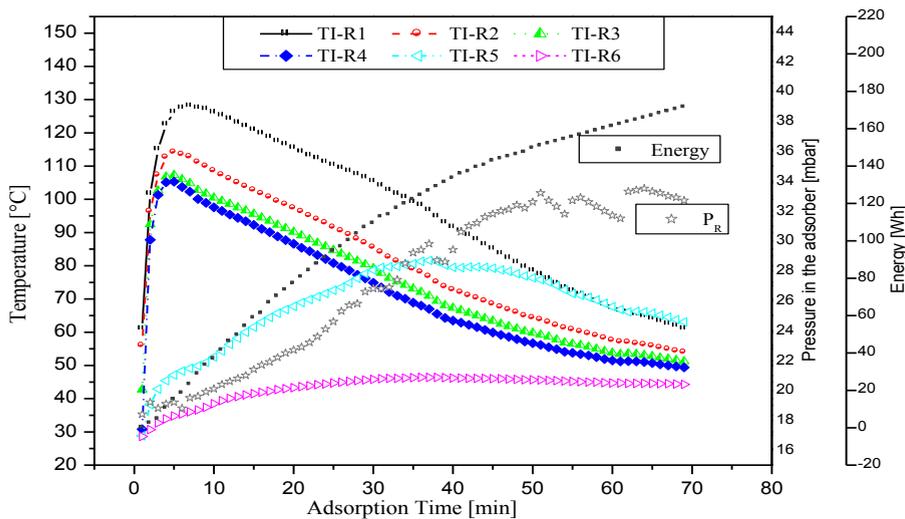


Fig. 4. Temperature, pressure, energy and water level with respect to adsorption time

the release of high temperature thermal energy as a result of an exothermic reaction. As the adsorbent becomes saturated and the temperature within the bulk rises, adsorption is not as favourable and the heat release gradually decreases. While the temperature inside the reactor (R) falls down, equilibrium continues to drive the adsorption process although at a much slower rate since the adsorbent is becoming

saturated. It has been observed that the desorption process occurred at about the same rate as adsorption after almost 60 minutes initial delay to get the required desorption temperature.

Moreover, parallel to the work mentioned above, short-term durability tests were also performed to predict the long-term performance of the applied storage materials. The results revealed that some of the zeolites that have been identified in these studies possess good hydrothermal stability for higher charging and discharging temperatures up to 200 °C. Related results on short-term cyclic adsorption/desorption tests in low temperature range, 90 - 120 °C, showed also a satisfactory regeneration for the composite materials. For such cyclic tests, the adsorption/ desorption procedure was repeated five times; thereby the adsorption performances of the material and the efficiency of the process were compared with the first cycle.

### 3.2. Experiments in advanced lab-scaled test rig (15 L)

Based on the results obtained from experiments with the 1.5 L lab-scaled test rig, different experimental investigations have been also carried out using the 15 L lab-scaled system to test different arrangements of the inner components of the storage module particularly that of the heat exchanger and gas channel with respect to the achievable performance, which is the heat output. To manage this, the interior of the storage module or the module as a whole has been made to be easily re-constructible. First tests were performed with different types of heat exchangers. Two adsorbents that have been identified in the former mentioned studies were selected as the adsorbent of choice for these series of experiments. As an example, performances of the two different heat exchanger (HX) configurations with 3- and 7-fins during adsorption process were compared here. In Fig. 5 some results obtained from adsorption experiments done using these two heat exchanger configurations are shown respectively. Other important values that have been obtained from the test runs are the heating power, the evaporation rate and the heat transfer coefficient in the adsorbent bed and from the adsorbent bed to the heat transfer fluid. These parameters were directly calculated during the test runs. For further comparison purpose, the calculated oil heat power output is included in Fig. 5. In these test series the absolute values are not significant because the heat exchangers were not optimized for a high heat in and output. Moreover, the system was not insulated during these tests. The focus of the experiments was on comparing the different types of heat exchangers depending on the temperature profiles in the storage module and the heat in and output. However, the comparison of the test results using temperature and pressure profiles revealed clearly, that more favorable heat and mass transfer have been attained using the heat exchanger with 7-fins configuration as a result of the difference in surface area. Furthermore, the stable heat power obtained using the 7-fins heat exchanger confirms a better performance of this heat exchanger configuration compared to 3-fins ones. The corresponding results obtained during desorption revealed that the temperature difference between the heat source ( $T_{OR}/T_{OV}$ ) and the bulk in the storage module using the 7-

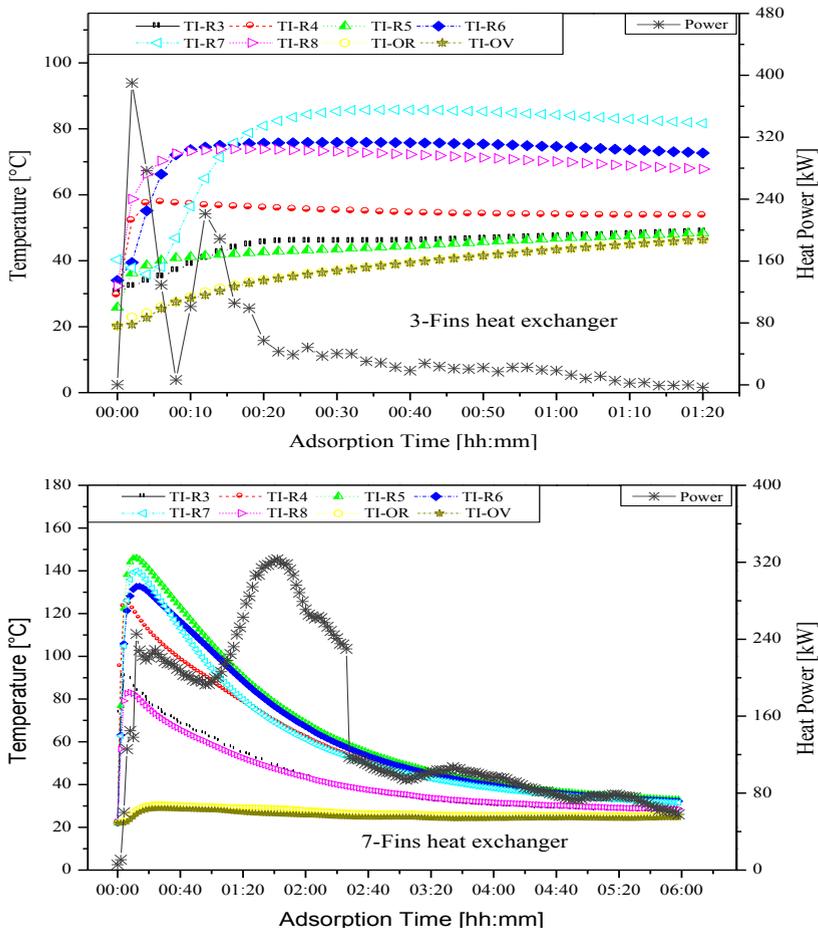


Fig. 5. Comparison of the temperature/pressure and heat power during adsorption using the 3- and 7-fins HXs

fins heat exchanger are lower than those obtained from the 3-fins ones. This reveals that the same effect, a better heat and mass transfer performance, has been also attained during desorption.

### 3.3. Results from the up-scaled system (750 L)

Based on the results obtained from the 15 L advanced lab-scale test rig, some experimental activities have been carried out using the 750 L up-scaled system. As it is described in section 2.2, due to the low moisture content ( $< 1\%$  w/w) of the applied storage material, the measurements were started with the first adsorption cycle. The temperature courses with respect to the adsorption time at five points inside the storage module and at the oil inlet/outlet is shown in Figure 6a. To achieve equilibrium in the system, the adsorption had been carried out in two days. The temperature and water level fluctuations observed (Fig. 6b) during the adsorption measurements were due to the initially manually operated main valve that has been frequently closed ( $MV = 0$ ) and opened ( $MV=1$ ) to keep the water level in the E/C constant. Despite these fluctuations, the average heat power is almost stable over a longer process time.

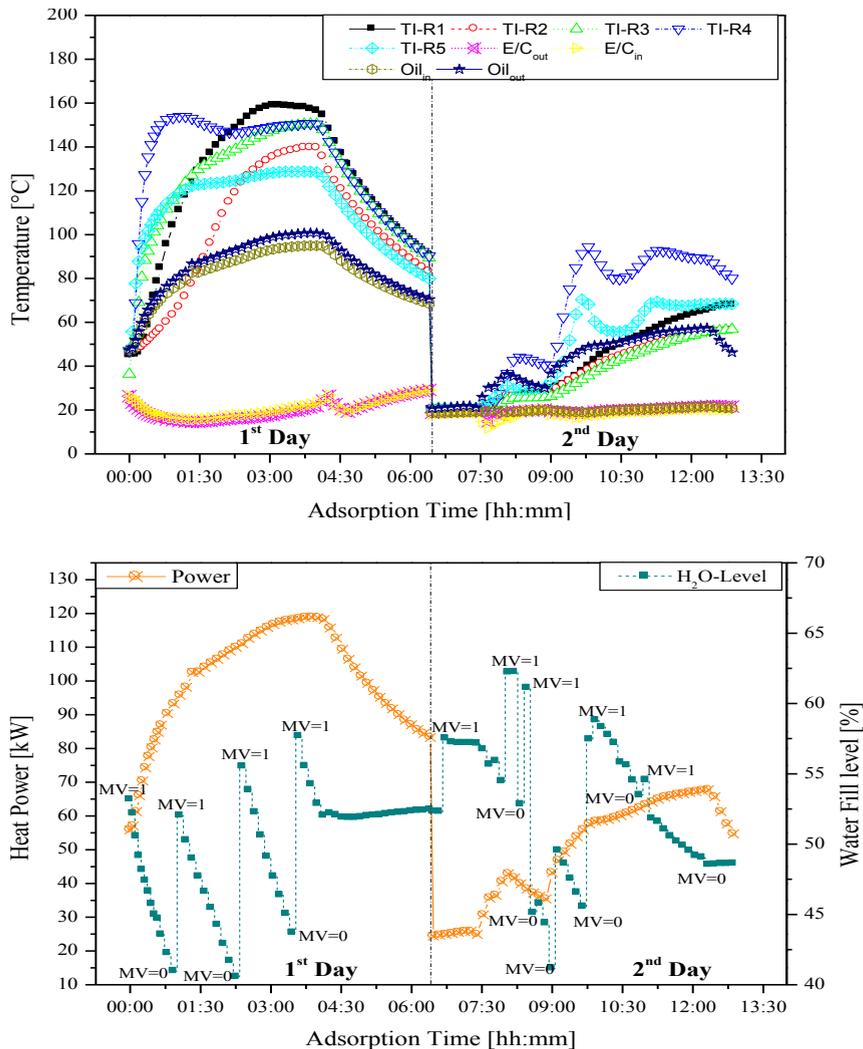


Fig. 6. (a) Temperature during adsorption in the up-scaled system; (b) Heat power and adsorbed water

Upon completion of the first adsorption cycle, the measurement was continued with the first desorption cycle. For this, the oil was heated to 200 °C and was introduced into the storage module through heat exchanger. After attaining the required pressure difference between the storage module and the E/C, desorption was started. However, shortly after, the storage module is evacuated and the pressure reduced from about 100 mbar to 10 mbar. This specific feature indicates that there is still significant amount of rest gas in the system, which has already hindered the adsorption process before. Then after desorption process was started once again. The desorbed water is condensed at 15 °C in the E/C. From the temperature plot (Fig. 7) one can see that the adjusted desorption temperature ( $T_D = 200$  °C at 24 kW oil thermostat) has been attained approximately after three hours. However, the results stated here show a relatively lower temperature gradient between the thermo-couples at different positions in the large-scale system compared to 15 L lab-scale test rig ones. This can be either as a result of a better heat transfer

within the system or due to the relatively longer heat exposure time that led to a more favourable heat distribution over the whole storage module.

To summarize the result part of this paper, a final and approximate system comparison (Table 2) has been done between the three different scaled storage test systems. For a comparison purpose, the result from dynamic adsorption has been also included.

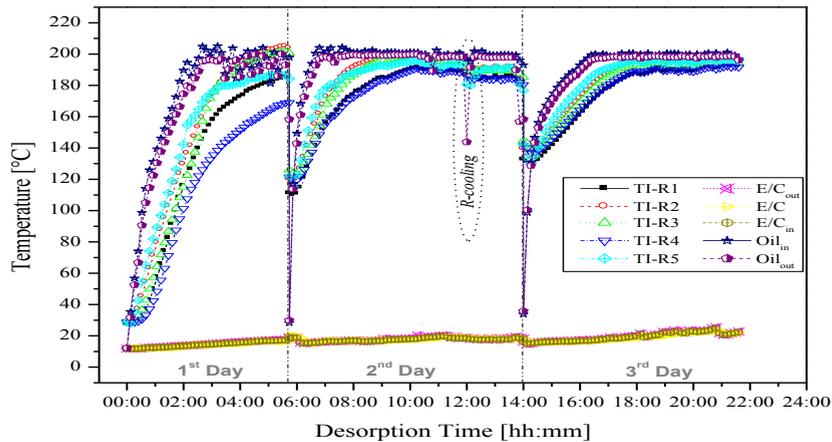


Fig. 7. Temperature profile during desorption in 750 L up-scaled system

Table 2. Summary of the system comparison

System	Specific Heat Storage Capacity [Wh/kg]	Specific Heat Power [W/kg]
static/dynamic adsorption	300 - 360	-
Lab-scale 1.5-Liter test rig	160 - 220	(60-240), not so stable
Lab-scale 15-Liters advanced test rig	180 - 240	45 – 66
Up-scaled 750-Liters storage reactor	(150 – 220) estimated	(19-50)

#### 4. Conclusions and outlook

From the tests carried out in 1.5-liter lab-scale test rig it was possible to get detailed adsorption characteristic features of different sorption materials to identify some suitable materials as well as important process conditions such as the temperatures and pressure ranges with respect to the storage density and the power output. Different heat exchanger concepts were tested and optimized using a flexible lab-scale 15-liters test rig. The result was a new heat exchanger configuration that showed a more than 60 % higher heat power rate than measured with standard heat exchangers in the bulk (reference: parallel copper plate heat exchanger). The concept comprises a combination of several measures to increase the storage density by improving the mass flow and the heat conduction of the adsorbent bulk. At the same time the loss of storage volume was low. As the last step, this improved concept was applied to develop and build fully functional storage system with about 750-liters storage volume and with a new heat exchanger design. The commissioning and testing of this large scaled system revealed quite satisfactory results, even though some scaling effects were observed. Furthermore, it is possible to control the storage process and to adopt the heat store to different temperature levels regarding the heat source as

well as the heat consumer. The technology appears to have a number of advantages for the future application in industrial processes and heating applications especially in combination with solar thermal systems. Thus, the short term testing phase with the up-scaled system will be continued throughout to get more practical experience and results with different process parameters. Moreover, it is planned to test the system at different sites using energy sources from solar thermal collectors and CHP plants to intensify the so far experience and to demonstrate the technology under real conditions.

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