# Seasonal thermochemical heat storage: first measurements on a falling film tube bundle laboratory setup.

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#### Abstract

Thermochemical energy storage in aqueous sorbents is a promising technology for long-term application. In an absorption system the absorption-desorption and evaporation-condensation heat and mass exchangers form the power unit whereas the tanks containing the sorbent (aqueous solution) and the sorbate form the capacity unit. An experimental test rig was built to perform and investigate the processes of absorption and desorption. The high number of different sensors permit the assessment of the processes. First results show a good monitoring of the data in the power range of 1 kW, which allow to compare different heat and mass exchangers together. The tube bundle heat and mass exchanger of the power unit is manufactured in three different versions. Plain tubes are used for a reference. For comparison, the heat and mass exchanger has either corrugated tubes - to increase the surface wetting - or tubes wrapped with ceramic foams. These measures are to increase both, the surface wetting of the tubes and the residence time of the sorbent in the sorbate vapor. In a further step, the gained measurement are foreseen for improving the numerical model (scaling method to higher power for building application).

Keywords: absorption, desorption, sodium hydroxide, seasonal storage, thermochemical compact heat storage

# 1. Introduction

More than 1/3 of Switzerland's energy demand is currently used for heating applications. Nowadays, 64 % of this heat is still produced by non-renewable sources like gas or oil (BFE, 2018), which could be replaced by solar energy applications or in general by renewables. However, the contrast between availability of solar energy produced heat in summer and demand in winter can only be remedied by seasonal thermal storage. A promising technology to store heat from summer to winter is the seasonal thermochemical energy storage with aqueous sorbents. Its main advantage is the high energy density and the loss free energy storage over time (N. Yu et al., 2013).

For such type of storages, during summer, heat from a solar thermal system is used in a desorption unit to raise the sorbent concentration (partial vaporization of water). While the concentrated sorbent is stored until winter in a separate tank, the water vapour leaves the desorption unit (D) driven by the vapour pressure difference and is condensed in the condensation unit (C) –. The condensation heat is released to the ambient (regeneration of a borehole) whereas the condensed sorbate is stored in an external tank. As long as no vapour reaches the high concentrated sodium hydroxide in the tank, the energy can be stored without losses. In winter, the reverse process is performed: the condensation unit serves as an Evaporator (E) and the low temperature heat from the borehole is used to vaporise the sorbate. As the whole processes in the system works at sub-atmospheric pressure, the sorbate boiling occurs at low temperature. The absorption of sorbate in the high concentrated sorbent takes place in the Absorber (A) and the heat is released at a significantly higher temperature level (foreseen use: building heating applications by radiant floor). The low concentrated aqueous sorbent (sodium hydroxide etc.) solution is stored until the regeneration process is started in summer.

Water vapour is used for the sorbate whereas a salt solution like lithium bromide, lithium chloride or, less expensive, sodium hydroxide can serve as a sorbent. The current paper focuses on the first measurements gained on an in-house built prototype designed to investigate the performance of a closed sorption heat storage using sodium hydroxide/water as sorbent/sorbate working pair.

# 2. Experimental test rig description

#### 2.1. Experimental set up

Fig. 1 shows a CAD view of the absorption-desorption test rig. It comprises a power unit with absorber-desorber (A/D) and evaporator-condenser (E/C) heat and mass exchangers. The three tanks underneath the power unit are for the sorbate (water) and for the high and the low concentrated aqueous sorbent.



Fig. 1: Front CAD view of the experimental setup (left) and exploded view of the heat and mass exchanger units (right).

Because of the seasonal separation of the processes - absorption in winter and desorption in summer – these two processes are at the current state of work unified in one chamber and build as one tube bundle (a compromise to reach high energy density). To analyse the absorption-desorption processes and not to limit it, the E/C unit is overdesigned.

#### 2.2. Measurement system and procedure

Due to experience gained on the operation of a former test rig (Daguenet-Frick et al., 2017) the instrumentation concept was improved and extended on the current test rig. This later enables to evaluate the process determining values (exchanged power, amount of condensed/vaporised water for example) by different ways and includes:

• 40 temperature sensors (all calibrated Pt 100 sensors) for the temperature measurement in the Heat Transfer Fluid (HTF) loops as well as on the surface of the tubes constituting the heat and mass exchangers (sorbent and sorbate temperatures).

- 5 piezo-resistive pressure transmitters (one in each chamber/tank)
- 4 flow rate measurement (2 magnetic inductive sensors, 1 Coriolis sensor and 1 oval-wheel-sensor) to measure precisely the flow rates in each of the HTF, sorbent and sorbate loop
- 3 radar level meters (tracking of the tanks filling in real time)
- 2 density measurement sensors (precise measurement of the sorbate concentration at the inlet as well as at the outlet of the A/D unit)

• 1 precision balance (assessment of the water quantity that is vaporised / condensed)

Continuous recording of the signal of all these sensors is implemented (data logging) and, for one process measurement point in steady state conditions, the boundary conditions are stabilised within a 15-minute (set of 900 measurement points in steady conditions, one per second). Processing of each measurement point consists in the calculation of some values (primarily heat transfer values) and time averaging the whole data set. For each value, the uncertainties (typically the "error" bars for each point of Fig. 2) stems from a statistical calculation (calculated confidence interval depending on the number of measurement for one data point).

#### 3. Measurements campaign

#### 3.1. First experimental measurements – facility function tests

The aim of the current facility is to investigate the absorption process i.e. the storage discharging, as it is currently limiting the power. Specially optimized A/D tube bundle were developed (textured tubes, use of ceramic foams...) and will be characterised and compared with the smooth (plane) tube heat and mass exchanger on this facility. Therefore, one main point at the end of the commissioning was to check that the E/C unit is not limiting the heat and mass exchanges. For this purpose, the influence of the recirculated volume flow rate of sorbate (liquid water) on the exchanged heat is shown on Fig. 2 for both desorption and absorption process.



Fig. 2: evolution of the power on both A/D and E/C tube bundle in function of the sorbate volume flow rate recirculated on the E/C unit for both desorption (left graph) and absorption (right graph) processes.

According to the left graph of Fig. 2, before thermal insulation of the E/C unit, this recirculated volume flow rate had some influence on the heat exchanged on the C side at room temperature  $T_{room}$  of 25 °C and condensation temperature  $T_{E/C}$  of 15 °C. Regarding this result, the E/C unit was thermally insulated. The second graph of Fig. 2 stems from afterwards performed measurements (same value of parameters  $T_{room}$ ,  $T_{E/C}$ ). Even if some minor influence of the volume flow rate can be observed on the evaporator power, the power on the absorber remains quite constant. However, despite of thermal insulation of the E/C unit as well as of the water tank and the sorbate pipes, it turned out that the E/C loop exchanges a lot of heat with the surrounding. In fact, the sorbate recirculation lead to a huge heat exchange area in comparison to the A/D loop where the heat exchanges with surrounding are negligible. For this reason, in the following measurements performed and analysis of the results, the power measured on the A/D unit will be privileged.

#### 3.2. Influence of the sorbent volume flow rate

The left side of Fig.3 shows the influence of varying sorbent volume flows on the absorption power. The graph on the right hand side shows the associated sodium lye concentration difference. The temperature difference between inlet temperature of the HTF at the A/D and E/C unit ( $\Delta T = T_{i\_AD\_in} - T_{i\_EC\_in}$ ) was either 10 K (triangle dots) or 20 K (square dots) and the evaporation temperature was kept constant ( $T_{i\_EC\_in} = 15$  °C). On the right graph, the concentration difference measurement shows large uncertainties. Indeed, for this measurement campaign the density sensor at the outlet of the reaction zone showed a fluctuating behaviour. It is assumed that the first version of the density sensors implemented on the test rig, based on the Coriolis principle were easily affected by external perturbation like microbubbles of vapor or non-condensed gas transported away by the sorbent.

To compare the measurement data and test the reproducibility, the first and last measurement point in a campaign of the day were conducted with a sodium lye volume flow of 54 ml/min (temperature difference of 10 K). The reproducibility is very good as the uncertainty bar covers the slight data point shift, which occurred during the measurement.



Fig. 3: absorption power (left) and concentration difference (right) in function of varying sodium lye volume flows at 10 and 20 K temperature difference between A/D and E/C unit for the smooth tube heat exchanger (HX).

The absorption power increases with increasing sodium lye volume flow. The higher flow does improve the wetting of the heat exchanger tube surfaces as well as turbulence on the tubes and as a result, the power increases according to logarithmic trend lines (doted lines in the graph). In the same time, the concentration difference decreases linearly with increasing volume flow rate, probably due to the reduction of the residence time of the sorbent in the heat and mass exchanger i.e. the sorbate vapour.

In general, the same trend is visible at both temperature difference levels. With high temperatures at the absorber HTF inlet ( $\Delta T = 20$  K), a slightly lower absorption power (about 10%) can be observed than for  $\Delta T = 10$  K. The achieved concentration difference is also affected by the temperature difference (the lower the temperature difference is, the higher the concentration difference  $\Delta wt$ ). However, this dependence is reduced at high sorbent flow rates; it seems that in this case the pressure differences between A/D and E/C (linked with the temperature difference itself) have less effect on the efficiency in comparison to the sorbent volume flow rate.

Practically, depending on the sorbent volume flow, different flow modes over the heat exchanger can be achieved. As the volume flow (resp. Reynolds number Re) increases, a transition from droplet to column or even sheet flow can occur (Roques and Thome, 2003). The increase of the Re number is linked to a rise of the turbulence but from a certain given Re number the wetting area can't be further increased whereas the residence time can even be reduced. However, in the considered test rig, the pump limits the volume flow rate and in these conditions, the droplet mode prevails. High sodium lye mass flow rates enable to increase the absorption power but on the other hand, this high mass flow rates are linked with a reduction of the concentration difference. As this concentration difference  $\Delta c$  is directly linked with the compactness of the thermochemical storage (the higher  $\Delta c$  the higher the stored energy), a compromise between power and concentration decrease will have to be found regardless of the heat exchanger (HX) shape.

#### 3.3. Influence of HTF volume flow on the Absorber

On the left hand side of Fig. 4, the absorption power and the HTF outlet temperature in function of the HTF volume flow rate are shown. The dotted red line indicates the transition from laminar to turbulent flow inside of the textured tubes of the A/D unit. On the right hand side, the influence of the heat transfer volume flow on the



sodium lye temperature (maximum reachable temperature in adiabatic conditions) and heat transfer fluid outlet temperature are shown. The temperature of the sodium lye was averaged over the heat exchanger.

Fig. 4: comparison of the absorption power (left) and the associated temperature difference (right) as a function of the HTF volume flow rate for the textured tube heat and mass exchanger.

According to (Rotta, 1956) a transition from laminar to turbulent flow begins, when the Reynolds number exceeds 2300 inside of a tube (volume flow rate above 45 L/h, for the considered geometry). This transition explains the slope discontinuity of the linear regression observed on both graphs of Fig. 4. The absorption power increases with increasing heat transfer fluid volume flow rate. On the other hand, the outlet temperature decreases as, by a constant temperature difference ( $\Delta T = T_{i\_AD\_in} - T_{i\_EC\_in}$ ), more energy can be transported out of the system by increasing fluid flow rate. For the final application, an optimal working point (compromise between output power and HTF fluid temperature) will have to be found.

At the minimal fluid flow rate, the stagnation temperature of the sorbent could be measured and is around 50 °C. In these conditions, the HTF temperature could not be measured precisely with the current test rig. In fact, the temperature sensors are placed to measure the temperature at the outlet of the tubes and not directly in the heat exchanger tube itself. However, as 50 °C is reached by the sorbent, a maximal temperature lift of 35 K between the evaporator HTF inlet temperature and the absorber HTF outlet temperature is practicable. With a borehole as low temperature heat source, the system may be de facto used at least for building heating applications at low temperature when not for pre-heating of domestic hot water.

3.4. Influence of the temperature difference between absorber and evaporator inlet for smooth and textured heat exchanger

In this section, measurement of both, smooth and textured version of the A/D heat exchanger are shown. The smooth (triangle dots) and textured (square dots) heat exchangers are compared and their absorption power is shown in Fig. 5 on the left hand side. Furthermore, the concentration difference due to absorption at different temperature differences between the A/D and E/C unit is shown on the right hand side.

As written in section 3.2, the first version of the density sensors implemented on the test rig were easily affected by external perturbation like microbubbles of vapor or non-condensed gas carried away by the sorbent. However, this prototype version of density sensors were replaced by commercial ones, which turn out to be much more reliable, before the textured tube experiments were conducted. The concentration measurement error bars are consequently smaller for the textured tube experiments.



Fig. 5: Comparison of the absorption power (left) and the associated concentration difference (right) as a function of the temperature difference for the textured and smooth tubes.

As expected and already explained in section 3.2 the absorption power decrease with increasing temperature difference. With the textured tube shape heat exchanger, an absorption power up to 20 % higher was achieved compared to the power with the smooth tube version. The enlarged surface does increase the residence time. In addition, the wetting of the tubes itself improved as it can be seen on Fig. 6. The droplets fall more along invisible tracks for the smooth HX, whereas for the textured HX the surface is wetted over its full visible length. Both residence time and wetting enhancement results in a higher concentration difference and therefore in a higher absorption power.



Fig. 6: evolution of the wetting on both tube bundle types in the A/D unit. Smooth tubes on the left (droplet mode) and textured on the right (transition to column mode). A higher wetting of the textured tubes at the same volume flow can be observed.

Despite of the increase of the absorption power noticed with the textured second generation of A/D heat exchanger, the aimed power of 1 kW was not reached for the absorption process. This goes also along with the concentration difference: a maximal reduction of 7.5 wt.% was achieved instead of the 20 wt.% targeted. In contrast, desorption measurements on the textured A/D showed that both expected power as well as concentration difference can be reached in this working mode and design. This shows that the insufficient results obtained in the absorption process are linked with the high viscosity of the high concentrated sodium lye solution. This viscosity itself prevents a good wetting of the tube bundle surface as well as appropriate residence time inside of the heat exchanger (exposition time of the sorbent to the sorbate vapour). To challenge both of these weaknesses, it is foreseen to investigate the behaviour with a third generation heat exchangers whose tube bundle is covered by ceramic foam. These experiments will be done as soon as the observed problem of outgassing of the foam is solved.

# 4. Conclusion and Outlook

The experiments were focused on the investigation of the absorption power for smooth and textured tube shapes. In fact, the absorption power measured was 20 % higher with the textured tube surface compared to the smooth tube design. The better wetting and the longer contact time of the sodium lye with the water vapour results in a higher concentration decrease, which leads to the higher absorption power measured and thus overall to a better compactness of the thermochemical storage. Apparently, the main influencing parameter on the absorption power is the high viscosity of the NaOH-H<sub>2</sub>O solution at low temperature and high concentration, which prevent the smooth heat exchanger to be completely wetted as well as to reach an appropriate residence time of the sorbate in the heat and mass exchanger. The high viscosity may also negatively affect the concentration gradient in the fluid on the tube surface, preventing the absorption of water vapour in and mixing the sodium hydroxide film.

The next step in the further investigations will be to implement a HX with ceramic foam tube shape in the laboratory test rig. This should allow achieving a higher absorption power with the same reactor size and an assessment will show the advantage. Another step forward could be the use of surfactants also to increase the surface wetting and the contact time of the sodium lye with the water vapour.

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