

Closed Sorption Seasonal Thermal Energy Storage with Aqueous Sodium Hydroxide

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Abstract. In this paper, a 1 kW closed sorption heat storage prototype is presented. The two main processes (charging and discharging) occur under reduced pressure. During the charging process, the thermal energy produced by the solar collectors in summer is used to partially vaporize the water contained in a diluted sodium hydroxide solution (NaOH). Then, the concentrated aqueous sodium hydroxide solution and the water are stored at room temperature in separate tanks until the discharging process. During discharging, ground heat is used as a heat source to evaporate the stored water under sub-atmospheric pressure in the evaporator. In a separate chamber, heat is produced during the exothermic process of water vapor absorption into the concentrated NaOH solution. The heat is then transferred to a working fluid that can be used, for example, in floor heating applications. Sodium hydroxide has a high water affinity; nevertheless, the fluid wetting on the heat and mass exchanger influences the absorption process efficiency. Different experimental methods to improve the surface wetting like surface modifications (structuring, use of ceramic foams) and fluid properties tuning (use of surfactants) are presented. The development of the structured surfaces and ceramic foams enhances the heat transfer and thus reduces the size of absorber unit.

Keywords: Seasonal thermal energy storage · Aqueous sodium hydroxide · Surface wetting · Ceramic foam · Surface texturing

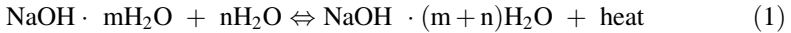
1 Introduction

In Europe, around 50% of the energy demand is used for heating, cooling and hot water applications. Seasonal thermal energy storage (TES) using solar thermal collectors in summer time could ensure the required thermal energy, while decreasing the need for fossil fuels.

Different materials with high energy capacity are investigated for thermal sorption storage [1–6]. Not only the materials characteristics (e.g. water vapor uptake, crystallization) are relevant, but also the operating parameters (e.g. temperature for charging, discharging, condensation and evaporation). Recommended operational parameters used for sizing a domestic seasonal solar thermal storage in Switzerland are: maximum solar collector temperature: 95 °C, heat sink temperature: max. 35 °C, space

heating (floor heating) return temperature: 26 °C, domestic cold water: 10 °C, sorbent storage temperature: min 10 °C [4].

Water vapor absorption in aqueous solutions like sodium lye (Eq. 1) achieves theoretically a significantly higher volumetric energy density compared to sensible water storage [8].



A full scale 10 kW demonstrator storage of a closed sorption TES using sodium lye was designed and built in the EU FP7 project “Combined development of compact thermal energy storage technologies - COMTES” [7, 9–12]. The system is based on liquid state absorption heat pump and it is operated under vacuum conditions. The main components of this system are: solar thermal collectors, reaction zone with heat exchangers for discharging/charging processes (absorber/desorber, A/D), a low temperature heat source and a heat sink for the evaporator and condenser (E/C) unit, storage tanks for the sorbent and the sorbate, a small domestic hot water store for having enough thermal power during DHW preparations and a control system [1].

Investigations performed in the COMTES project have shown a lower efficiency compared to the theoretical value during the absorption phase (storage discharging) [8]. A poor wetting of the A/D unit tube bundle (AISI 316L) and a short residence time of the liquid sorbent (concentrated aqueous NaOH solution) in the water vapor are considered the main causes for this behavior. Thus, a 1 kW prototype is developed in a consecutive Swiss national R&D project (ABSTOREX) to optimize the reaction zone unit.

2 Development of a 1 kW Thermochemical Storage Prototype Using Sodium Hydroxide. System Design - Reaction Zone

A liquid sorption energy storage concept is used for developing the 1 kW thermochemical storage prototype using sodium hydroxide. The main components and also the charging and the discharging processes are represented schematically in Fig. 1 (charging process) and Fig. 2 (discharging process).

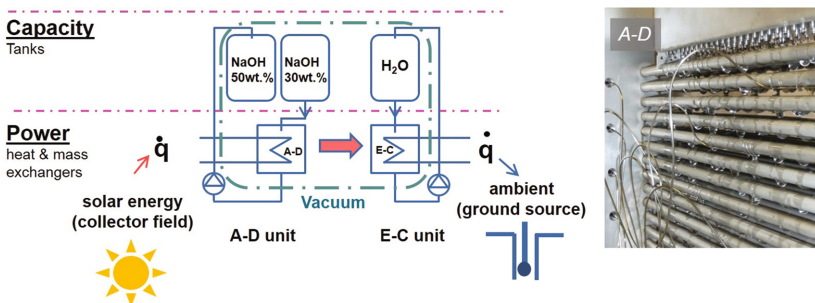


Fig. 1. Charging process in summer time (desorption process)

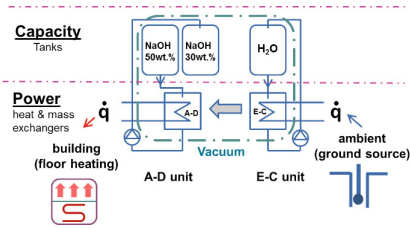


Fig. 2. Discharging process in winter time

The reaction zone is consisting of two main units: A/D (absorber/desorber) and E/C (evaporator/condenser). The system was designed to allow the separation of capacity (which is given by the volume of the storing tanks for the sorbent - NaOH and sorbate - H₂O) and power (given by the heat and mass exchangers' active area).

The charging process occurs in summer when the heat from a collector field is used to partially evaporate the water from the liquid sorbent, a diluted sodium hydroxide solution (30 wt.%). The process takes place in the desorber unit, which consists of a falling film tube bundle heat and mass exchanger. This chamber is used not only for the desorption process, but also for the absorption (discharging in winter). This combination of two process steps in one single chamber is possible because of the seasonally separation of charging and discharging. The concentrated sodium lye solution (50 wt.%) is stored without thermal losses until discharging process occurs. The latent condensation heat from the water vapors is released to a ground source (e.g. a borehole), while the condensed water is stored in a separate tank at room temperature.

A reversed process takes places during discharging. A low temperature thermal input (a ground source) is used for water evaporation under reduced pressure in the evaporator unit. By combining the concentrated sorbent with water vapor in the absorber unit, the stored heat is recovered. The TES unit can be used both for space heating and domestic hot water applications.

In the ABSTOREX project, a heat and mass transfer unit with low power consumption was designed. Different sorbent pairs with high energy density are investigated: NaOH-H₂O, LiBr-H₂O and LiCl-H₂O. The mass and heat transfer characteristics are determined for these thermal fluids. The results will permit scaling of larger units with correspondingly higher power.

The CAD design of the heat and mass transfer zone - the power unit and the sorbent and sorbate tanks - the capacity unit - of the storage system is presented in Fig. 3.

Both the A/D and E/C units contain a fluid distribution manifold and a falling film tube bundle (Fig. 4, left). These components are in a vacuum tight container. A modular design was chosen for the easy replacement of the tube bundle flange (Fig. 4, right) in case of the absorber/desorber unit. This configuration allows testing several types of tubes and fluid modifications (surface texturing, different sorbents with/out surfactant addition) [13].

Outside on the hair pin tubes, under reduced pressure is flowing the aqueous sorbent (yellow arrows) driven by gravitational force. A uniform distribution of the sorbent over the first hair pin tube is given by a specially designed manifold. This consists of two coaxial tubes: the inside tube has two perforations on its upper side, the outside tube has equally distributed nozzles with a diameter tailored for an optimum liquid sorbent flow.

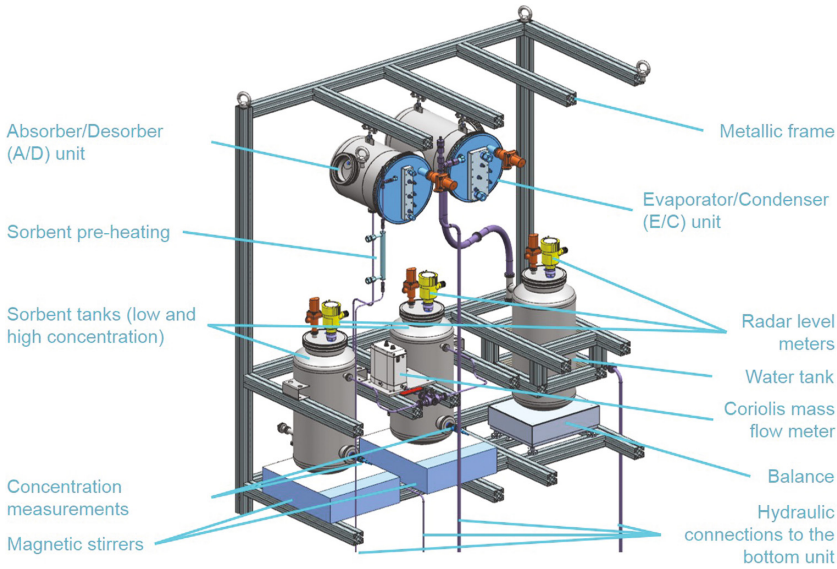


Fig. 3. Isometric view of the top of the facility with the heat and mass exchanger unit as well as the storage tanks

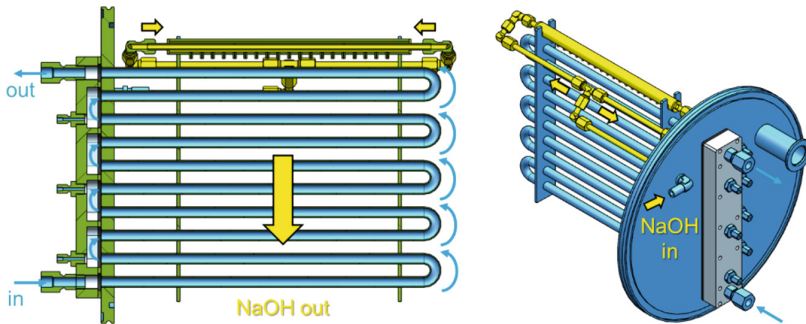


Fig. 4. Sectional view of the absorber/desorber heat and mass exchanger (tube bundle and flange in blue, manifold in yellow)

The sorption process of water in sodium hydroxide and consequently the produced heat is strongly influenced by the liquid sorbent wetting over the heat exchanger surface. Different experimental methods were used to improve the surface wetting of stainless steel tubes with concentrated sodium hydroxide solution [13–16]. Wetting is the ability of a liquid to maintain contact with a solid surface due to the intermolecular interaction between the liquid and particles from the solid substrate. The liquid spreads in order to lower its surface energy. Drops lose their spherical shape due to gravity. When the radius of the droplet is much smaller than the capillary length, the effects due to gravity are negligible and the drop deposited on the solid substrates maintain a

spherical shape. For NaOH 50% wt., the capillary length is 2.8 mm (at 20 °C). Small droplets in the range of tens of μL maintain their spherical form.

Better wetting is promoted when a large surface area is in contact with the liquid. Higher surface area is obtained by varying the surface roughness and mechanical texturing. However, not all types of surface fining (structuring) are appropriate to be used with concentrated sodium lye solutions - a highly viscous solution [13].

Moreover, the efficiency of the discharging process is strongly influenced by the residence time of the concentrated sodium lye solution in the water vapor. Results of the preliminary investigations regarding the use of ceramic foams with sodium hydroxide are presented in the following chapter.

3 Hydrophilic Porous SiC Foam for Increasing the Residence Time of the Sorbent in the Water Vapor

Silicon carbide (SiC) is an ultra-hard covalently bonded material. It is very stable and it can react with sodium hydroxide only in the presence of oxygen and at temperatures over 350 °C to produce sodium metasilicate. As in the ABSTOREX project, the working temperature is below 100 °C and the atmosphere is oxygen free (vacuum), SiC can be used to increase the residence time. The foam is manufactured as a tube, inside which the stainless steel tubes from the tube bundle are inserted (Fig. 7). Different porosities of the SiC foam were selected for testing, with porosity ranging from 10 to 30 PPI, where PPI (Pores Per Inch) represents the number of pores in one linear inch (length).

In a first step, the wetting behavior of the ceramic foam was assessed with two sorbent liquids which are used in the heat and mass exchanger:

- sodium hydroxide (NaOH), 50 wt.% in H_2O , density: 1.515 g/mL at 25 °C, surface tension: 116.72 mN/m;
- lithium bromide (LiBr), 54 wt.% in H_2O , density: 1.57 g/mL at 25 °C, surface tension: 86.1 mN/m.

Different volumes of aqueous solutions of NaOH and LiBr ranging from 100 to 1000 μL were used. The preliminary wetting experiments have indicated that all the tested ceramic foams have a hydrophilic behavior, both with concentrated NaOH (45 wt.%) and with LiBr (54 wt.%) solutions (Figs. 5, 6).

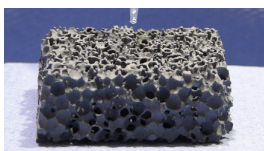


Fig. 5. Concentrated NaOH (45 wt.%) completely wets the SiC ceramic foam

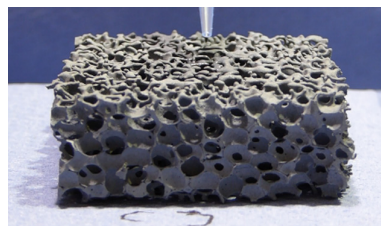


Fig. 6. Concentrated LiBr (54 wt.%) completely wets the SiC ceramic foam

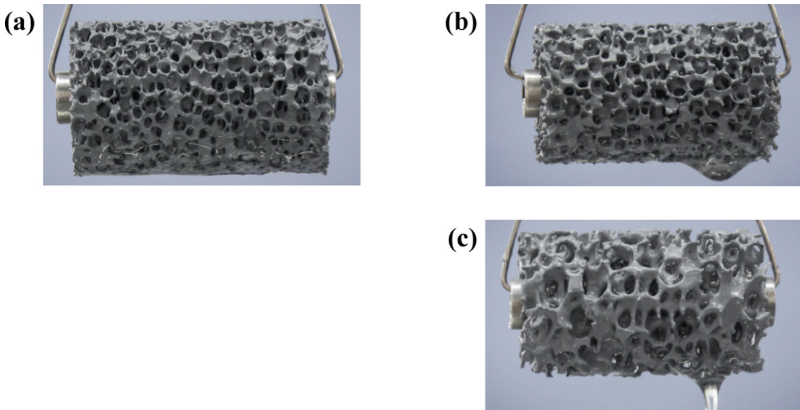


Fig. 7. Hydrophilic SiC ceramic foam with pores partially filled by concentrated aqueous sodium hydroxide. The porosity is ranging from (a) 30 PPI to (b) 20 PPI and (c) 10 PPI, where PPI represents the number of pores per inch

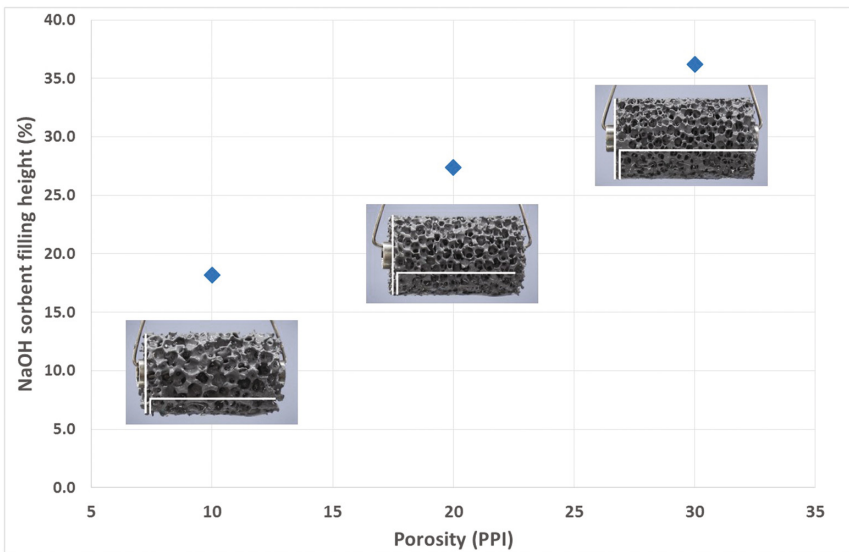


Fig. 8. Correlation between the ceramic foam porosity and sorbent filling height

A next step was to assess the effect of the ceramic foam on the residence time. Stainless steel tubes ($D_{ext} = 10$ mm, $D_{int} = 8$ mm) wrapped by ceramic foam ($D_{ext} = 50$ mm, $D_{int} = 10$ mm) with different porosity were immersed in concentrated sodium hydroxide solutions (45 wt.%).

Higher residence time is obtained for the sample with smaller pore size (30 PPI, Fig. 7a). Larger pores favor a faster flow of the concentrated sodium hydroxide solution, thus a lower residence time follows (Fig. 7c).

The filling height can be directly correlated with the ceramic porosity (Fig. 8). The accessible void was filled up with concentrated sodium hydroxide solution (50 wt.%). Then, the sorbent filling rate was assessed for the three sample with different pore size.

A larger number of small pores favour a higher filling height and also higher residence time (sample with 30 PPI).

4 Conclusions

Water absorption/desorption in a high volumetric energy density fluid, as aqueous sodium hydroxide solution, is an efficient method for compact seasonal thermal energy storage application. Previous experiments made in the EU funded COMTES project have indicated a lower power during the absorption (storage discharging) phase. This low performance can be explained by the poor wetting of the tube bundle of the absorber unit by the concentrated sodium hydroxide and the low residence time of the lye in the sorbate vapor phase.

The focus of our work is to develop a 1 kW absorption/desorption demonstrator unit using the falling film working principle with improved efficiency. One of the first steps is to optimize the heat and mass transfer at the tube bundle surface in the absorption process. This can be done by tailoring the surface wetting and increasing the liquid sorbent residence time in the water vapor.

Ceramic foams made of silicon carbide (SiC) were successfully tested for increasing the residence time of concentrated sodium hydroxide. Higher residence time is obtained for the sample with smaller pore size (30 PPI, where PPI represents the number of pores per inch). Larger pores favor a faster flow of the concentrated sodium hydroxide solution, therefore lower residence time is obtained in this case.

These results will be used to improve the tube bundle from the absorber/desorber unit. The SiC foam will be further tested by integrating it in the 1 kW prototype.

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