

# LONG-TERM HEAT STORAGE WITH NaOH

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## Abstract

To reach high solar energy fractions for building heat supply, several seasonal thermal storage techniques have been developed so far. Besides ground storage techniques, thermo-chemical techniques with high heat storage capacity and virtually no heat losses in the storage state are most promising. The paper deals with closed sorption systems and focuses on the concept with sodium hydroxide (NaOH) - water as the working pair. In an experimental prototype set up, heat charge and discharge processes of the storage under low pressure conditions were analysed and verified.

The storage capacity is limited by the temperature levels of the produced heat and by the solidification of the NaOH lye. Simulation results show that for charging the storage, solar heat can be supplied at 100°C, and that, compared to conventional water storage, the system volume related heat capacity could be increased by a factor of 6 for low temperature space heating (40°C) and by a factor of 3 for domestic hot water supply (65°C).

During the last months, the laboratory prototype was extended with a double-stage heat exchanger. Currently measurements to identify system parameters are carried out.

Future systems shall be built in one integral vacuum container, containing solution tanks, heat exchangers, piping and pumps.

## 1. Introduction

The aim of the 2000 Watt society is the reduction of the fossil fuel consumption in Switzerland by a factor 9 until 2150 to 2200 [1]. This goal can only be reached with rational use of energy and a shift to renewable energy sources. New building standards (like the passive house standard [2]) have only a fractional amount of the heating energy demand compared to older standards. This allows to cover the small residual energy demand for heating and domestic hot water by solar heat. So far, the use of solar energy has been limited by the semi-annual time shift between maximum gain and maximum heat demand. To overcome this limitation, various approaches of seasonal storage are explored. Basically, three main technologies can be distinguished: (i) large scale thermal energy storage (water, soil, and aquifer) [3], (ii) phase change material (PCM) based storage [4], and (iii) thermo- chemical storage [5].

With the first storage technology, heat is stored by a temperature change of a material with a high specific heat capacity per volume. For seasonal storage, extraordinary insulation of the vessel is required. The PCM storage technology uses the sub-cooling effect of Sodium Acetate. The sub-cooled liquid PCM is stored and can be forced to crystallize whenever heat is needed. With the crystallization, the solidification enthalpy is released and the produced heat is used for heating purposes. Thermo-chemical storage techniques stores heat by separation of chemical substances. To retrieve the heat, the

substances have to be recombined. In the field of thermo-chemical storage, a promising method for low temperature storage is closed sorption. This concept is based on sorption materials which, for heat output, absorb/adsorb the vapour of a solute (mostly water) and thus release the enthalpy of ab/adsorption.

## 2. Sorption heat storage

Thermo-chemical storage is an indirect way to store heat. The heat is not stored directly as sensible (i) or latent (ii) heat but by way of a physico-chemical process. Thermo-chemical storage systems can be classified by design (open/closed systems), by the reaction type (adsorption/ absorption), and by the number of phase changes. A detailed overview can be found in [5].

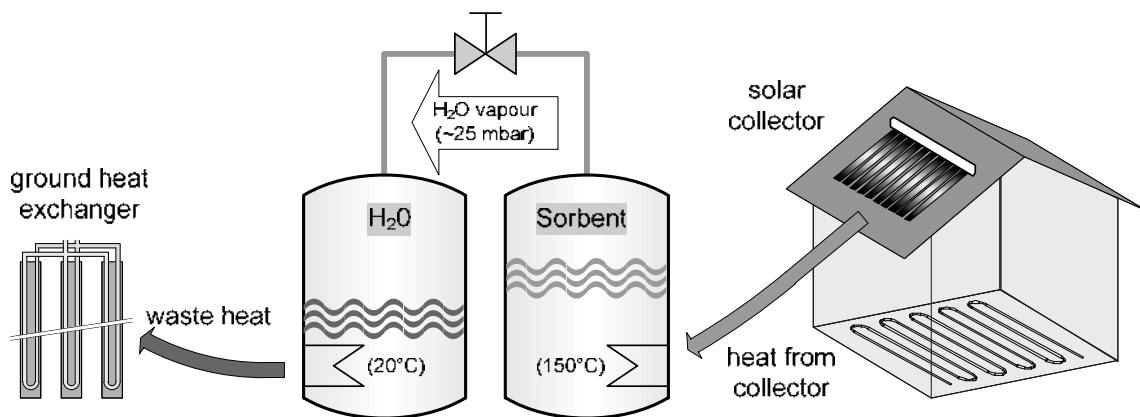


Fig. 1. Charging mode. Sorbent is heated up to evaporate the working fluid.

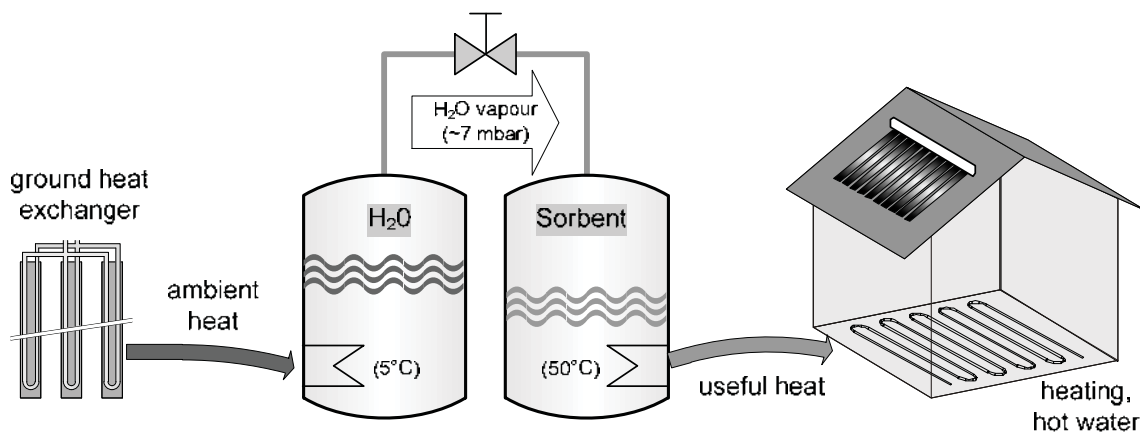


Fig. 2. Discharging mode. Vapour is absorbed by the sorbent

The working principle of closed sorption storage is illustrated in Fig. 1 and 2. During the charging phase, (solar) heat is needed to evaporate the working fluid. In closed systems, the working fluid

(mostly water) is condensed and stored in a separate vessel. The evaporation enthalpy obtained thereby is released to the environment. As long as a recombination of the agents can be prevented, no heat losses occur. In the reverse process (discharging mode), low temperature heat is taken from the environment to evaporate the working fluid. The vapour is absorbed by the sorbent, thereby releasing the evaporation enthalpy. The produced heat can be used for space heating or domestic hot water. This reverse process is going on until a status is reached, where the sorbent does no longer absorbs vapour. Closed storage systems typically run under vacuum conditions (meaning: air free environment) to speed up vapour transport and to minimise heat losses by convection.

Several combinations of sorbent and working fluid, called working pairs, are possible. An optimal working pair complies with the requirements and criteria listed below [5]. However, there is no working pair known which complies with all criteria. Therefore, the material selection has to be optimized. Work on the identification of suitable materials and designs for sorption storage are still in progress [6&7].

- The sorbent shall grant high uptake (kg sorbate/kg sorbent) of working fluid. If water is the sorbate (working fluid), the sorbent has a high selectivity for water.
- The working pair shall show high thermal energy density at operating temperature.
- Charging shall be feasible by heat provided at relatively low temperature.
- For solar heat use, a short regeneration time is needed (requires either a small saturation gradient in thick sorbent layers or thin sorbent layers, where the gradient is no criterion).
- To keep the heat exchanger small, high heat conduction in the sorbate and high heat transfer to the heat exchanger are required.
- To inhibit corrosion, the materials of the working pair ought to be chemically stable.
- The materials have to be easy to handle and non poisonous.
- An economically viable solution can only be realized with low cost material (low price per kWh heat energy stored and delivered).

This paper describes a project where sodium hydroxide (NaOH) - commonly known as caustic soda, soda lye, or sodium hydrate - has been selected as working pair, considering the following advantages (+) and disadvantages (-):

- + NaOH has a high uptake of water and therefore a high storage density.
- + Temperature levels for both charging and discharging match with the respective levels of the (solar) heat source and the demand side.
- + The NaOH lye is readily available, commercially employed, and available at low price.
- + The liquid NaOH lye forms thin films on the heat exchanger, and thus offers high heat transfer coefficients and short regeneration times.
- + NaOH is chemically stable.
- NaOH is caustic; measures to prevent unintended skin contacts must be taken.
- NaOH is corrosive (depends on the chloride ions density).
- NaOH crystallizes at high concentration, which has to be considered in the handling.

### **3. Design of the Sodium Hydroxide storage**

In contrast to the general description in Fig. 1 and 2 where the storage design shows a batch mode, the NaOH storage shall work continuously. The main functionality of such a system is transforming a heat flux to a mass flow (and vice versa) and storing the resulting products. To reach that goal, the functionalities of transforming and storing are separated (Fig. 3). To charge the storage, weak soda lye is pumped from a tank to the heat and mass exchanger area (process unit), where it is concentrated. The vapour produced is condensed. Water and concentrated soda lye are pumped to separate tanks and stored again. The storage is fully charged if the concentration of the soda lye reaches about 75%.

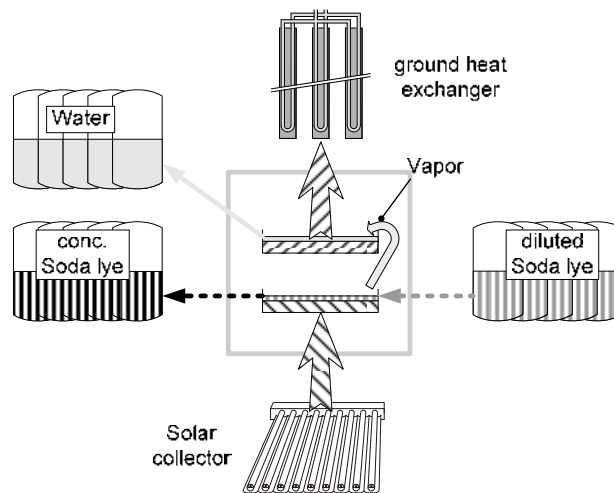


Fig. 3. Charging mode. Weak sodium hydroxide is pumped to the heat exchanger and concentrated. Water and concentrated soda lye are stored separately

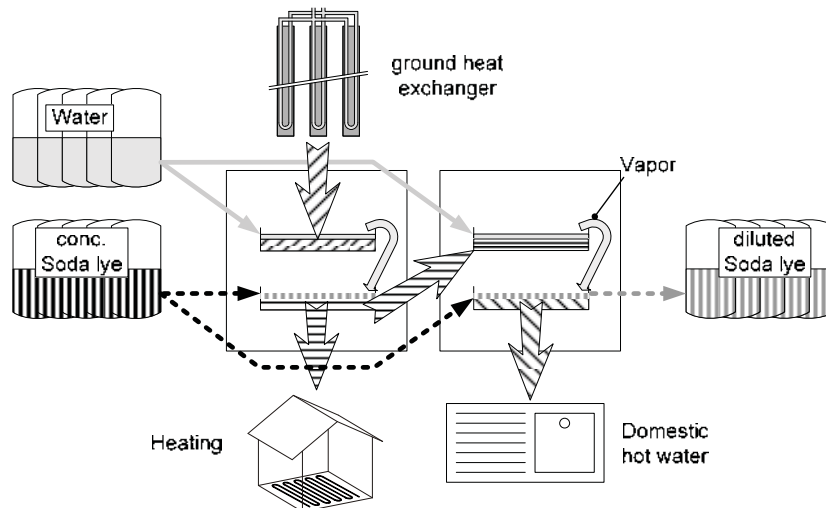


Fig. 4. Discharging mode. The produced heat of the first stage is used for heating or for evaporating water in the second stage. The high temperature heat produced in the second stage is used for domestic hot water.

To discharge the storage (Fig. 4), water and concentrated soda lye are pumped from the corresponding tanks to the first process unit (first stage). There, low temperature heat is produced either for heating or

for evaporating water in the second process unit (second stage). With a second stage, higher temperatures can be reached for the production of domestic hot water. Additionally, the usable concentration range for the sodium lye is higher, which results in a higher heat capacity of the storage. A detailed description of the working principle of the second stage can be found in [8]. However, heat losses during transformation occur twice, therefore the COP (coefficient of performance) is inferior to a system with only a single stage heat exchanger.

#### 4. Prototype test plant

A laboratory test plant has been set up at Empa. It consists of 4 storage tanks, two process units (also called stages) with integrated heat exchangers, dosing pumps, connections to cold and hot water supply, and a domestic hot water tank. The storage tanks with a volume of ca. 200 litres each are used to store water and solutions at different concentrations. In the high concentration solution tank, a heating unit is installed to allow for liquefying the crystallized solution, if required. To prevent corrosion, all metallic parts are made of stainless steel. The low temperature heat source is formed by Empa's chilled water campus grid. Hot water is supplied from an instantaneous water heater. The domestic hot water tank is used for intermediate storage of the produced domestic hot water (buffer store). Inside the process units, all absorption and desorption processes take place. The system is designed for gravity driven flow; therefore the dish shaped heat exchangers are staggered in a cascade (Fig. 5).

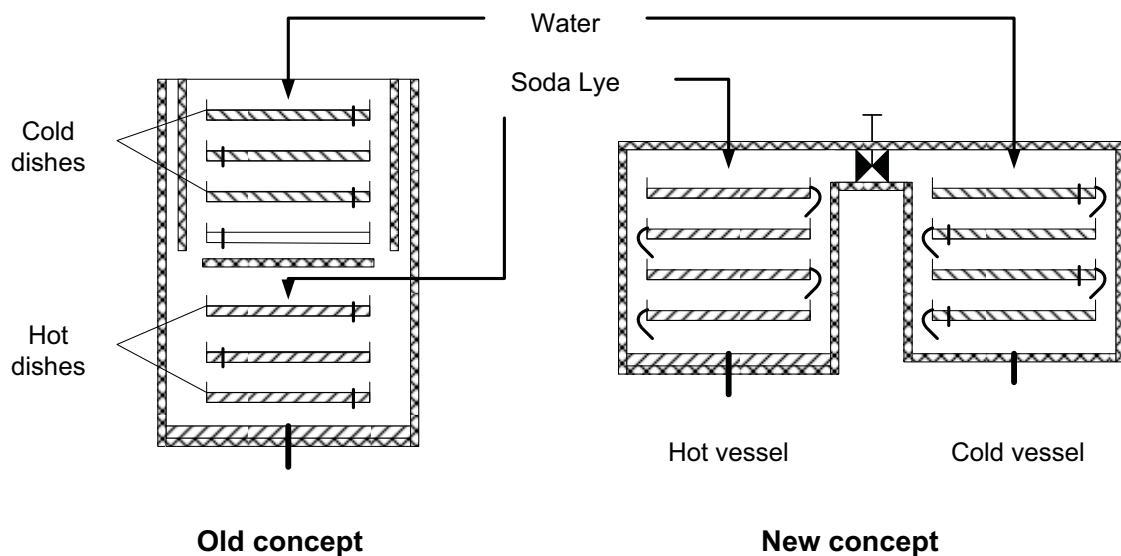


Fig. 5. Left side: First generation process unit (still used as the first stage). Right side: Improved process unit (used as the second stage).

Two different concepts of the process units with heat/mass exchanger have been realized. The first generation concept combines the hot (evaporation of vapour) and the cold (condensation) heat exchanger in one vessel. The advantages of this design are the very low pressure losses and the undisturbed vapour flow from the hot to the cold dishes. The disadvantages are high heat losses between the cold and warm side and serious problems with crystallisation effects.

The new concept of the process unit consists of two separate vessels and allows for producing and using high concentrated NaOH. The system has only small heat losses and crystallization can be circumvented. The large diameter of the connecting tube keeps the pressure loss between the cold and hot vessel also low.

In the present set-up of the test plant (Fig. 6), the first generation process unit is used as the first stage where typically low concentration NaOH is in use and the new process unit is used as the second stage. Currently, measurements are carried out to specify the TRNSYS simulation model parameters.

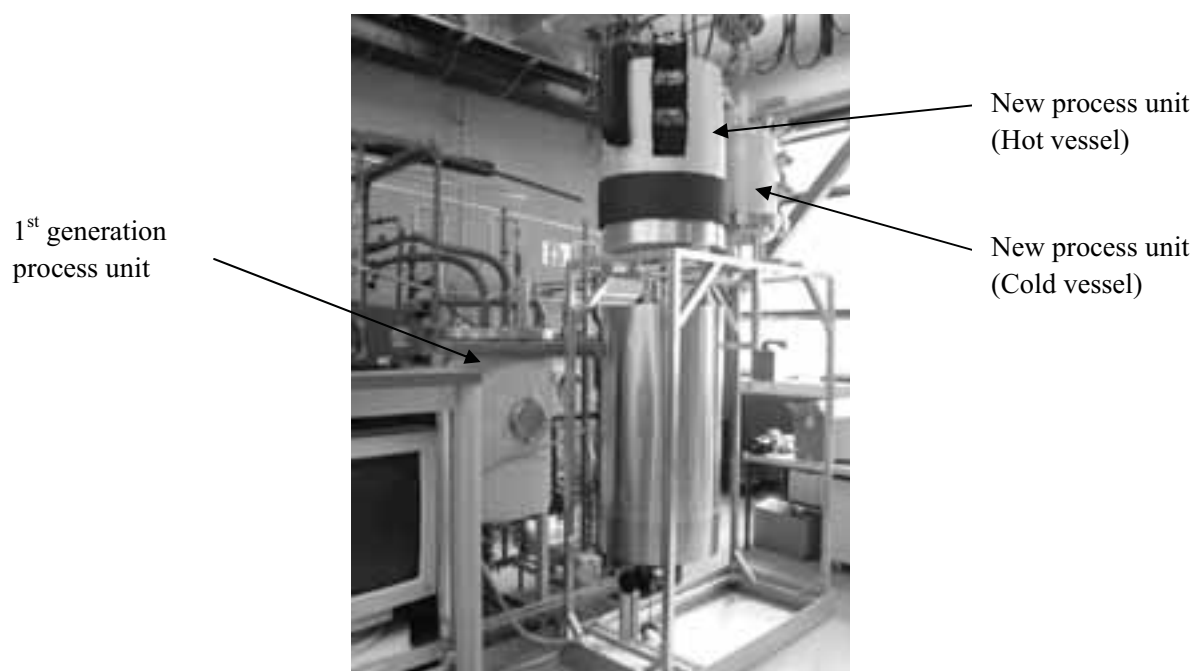


Fig. 6. Test plant with the new process unit.

## 5. Storage Performance

The process of the sorption storage was simulated by a simplified static model, implemented in Matlab, with which the storage density could be estimated and the application potential analysed. The energy density was basically calculated using the mean enthalpy of absorption per weight at selected temperatures. To be on the safe side for the performance prediction, several factors were conservatively assumed. Calculations were made for a single family home, of about 120 m<sup>2</sup> living space, and complying with the Passive House standard. As a result, a NaOH storage unit of approximately 7m<sup>3</sup> is required for 100% solar fraction. This value for the storage is the total volume of the unit in the building, including NaOH tanks, water tanks, and heat exchangers (but of course not the ground heat exchanger and the solar collectors). In general, for a hot water tap temperature of 65°C, the heat storage density is roughly 3 times higher compared to traditional hot water storage, and about 6 times higher for a tap temperature of 40°C for low temperature space heating.

The efficiency of a sorption storage system is indicated by the COP:

$$COP = \frac{Q_{Heat.out}}{Q_{Heat.in} + Q_{Auxiliary}} \quad (1)$$

Theoretically, good values of the COP are in the range of 0.6 – 0.8. The laboratory prototype currently reaches values in the range of 0.45 – 0.5. These rather low values are due to the non-optimised first generation process unit (with its high losses) and the use of the second stage.

Measurements show also that the charging process is about 3 times faster than the discharging process. A possible reason could be that during discharging, the vapour pressure in the process unit is only about one third of the value in the charging process. The mass transport (vapour flow) at the same pressure difference is therefore smaller. However, this is not considered as a severe limitation. The capacity of the heat exchangers has to be designed on the basis of the peak power delivered by the solar collectors, which is 4 to 5 times higher than the heating power demand of the building.

A new TRNSYS Type has been developed, allowing for dynamic storage performance evaluations. Currently a master student is implementing this type into the standard simulation cases as specified within IEA SHC Task 32. This will allow comparing the performance of this storage with other storage technologies.

## 6. Conclusions and outlook

A NaOH – water based process for long term storage of solar heat has been analyzed. The process has been demonstrated in a prototype plant with individually vacuumed storage tanks and two process units with built in heat/mass exchangers. The results show that, compared to conventional water storages, the system volume (tanks and heat exchangers) related heat capacity could be increased up to a factor of 6 for low temperature space heating with 40°C supply temperature. For domestic hot water supply at about 65 °C this factor is reduced to about 3.

Currently, measurements with the system are carried out to identify parameters for TRNSYS simulations. With building and system simulations, it shall be shown how the storage and the additional components (solar collectors, earth heat exchangers, buffer stores etc.) have to be dimensioned to reach 100% solar fraction.

In future, the system will be designed as one integral vacuum container, in which the whole storage system is placed, comprising multiple solution tanks, two process units (because of the double-stage system), and the necessary piping and pumps. Such, the vacuum container has not to sustain the highly corrosive environment of the NaOH lye and may be of conventional carbon steel. As the solution tanks are fully placed in vacuum they do not experience a high pressure difference and can be made of polypropylene. This will contribute to a cost effective system without corrosion problems.

## 7. Acknowledgements

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