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Eidgenössisches Departement für
Umwelt, Verkehr, Energie und Kommunikation UVEK

Bundesamt für Energie BFE

Schlussbericht 03.06.2016

NAOH-SPEICHER FÜR SAISONALE WÄRMESPEICHERUNG

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BFE-Vertrags- und Projektnummer: SI/500064-02

Content

Abstract

An essential part in the utilization of solar thermal power is seasonal storage. In the last years numerous developments have been made to achieve this. Most activities focused on storing sensible heat in a diversity of materials and shapes. All taking in account the high heat loss and large volume requirements associated. For this reason, most systems are not able to cover all the space heating and domestic hot water requirements in the cold seasons.

In the past years new possibilities have been analyzed, and in the scope of the International Energy Agency (IEA) Solar Heating and Cooling Program (SHC) Tasks 32 [1] and 42 new approaches have been studied. Utilizing the solar thermal power potential as a forefront player in reducing consumption of finite fossil fuels requires compact seasonal storage systems with no thermal loss during storage.

In the scope of this project, a NaOH sorption storage for seasonal solar thermal storage has been developed, built and tested. Rather than sensible thermal storage, this novel concept is based on the principle of the absorption heat pump operation. In this manner a theoretical energy density increase of 3 to 6 times compared to that of the sensible thermal water storage is achieved and the system is not susceptible to thermal loss during storage time.

This system was built in two steps, initially with one heat pump stage and then extended to a two stage system to increase the output temperature. Computer simulations accompanied this development in order to improve the design process.

Zusammenfassung

Die saisonale Speicherung spielt eine zentrale Rolle in der Nutzung der Solarwärme. In den vergangenen Jahren wurden zahlreiche Entwicklungen diesbezüglich unternommen, meist auf Basis der sensiblen Wärmespeicherung. Viele dieser Entwicklungen konnten Erfolge vorweisen, doch alle leiden unter kontinuierlichen Wärmeverlusten verbunden mit einem hohen Volumen. Die meisten Entwicklungen sind nicht in der Lage den gesamten Bedarf an Brauchwarmwasser und Raumwärme zu decken.

In den vergangenen Jahren wurden weitere Möglichkeiten in Betracht gezogen und im Rahmen vom IEA SHC Task 32 [1] wurden neue Ansätze überprüft. Um das Potenzial der Solarwärme zur Reduktion der Verwendung fossiler Brennstoffe umzusetzen, braucht es kompakte verlustlose Speicher.

Im Rahmen vom Projekt “NaOH Sorptionsspeicher für saisonale Wärmespeicherung” wurde ein solcher Speicherprototyp entwickelt, gebaut und getestet. Anstelle der herkömmlichen sensiblen Wärmespeicherung basiert dieses Konzept auf dem Prinzip der Absorptionswärmepumpe. Mit dieser Technologie lässt sich theoretisch eine 3 bis 6 fache höhere Energiedichte im Vergleich zur sensiblen Warmwasserspeicherung erreicht, und es entstehen keine Verluste während der Speicherung.

Die Systementwicklung unterlief in zwei Schritten, wobei anfangs eine einfache Wärmepumpenstufe realisiert wurde, die in einem zweiten Schritt mit einer zweiten Stufe erweitert wurde um die Ausgangstemperatur zu erhöhen. Unterstützend zur technischen Entwicklung wurden Computersimulationen erstellt.

Nomenclature

Abbreviations

ATES	Aquifer Thermal Energy Storage
COP	Coefficient of Performance
TCM	Thermo Chemical Materials
DHW	Domestic Hot Water
IEA	International Energy Agency
SHC Task 32	Advanced Storage Concepts for Solar and Low Energy Buildings
MATLAB	Numerical computing environment
PCM	Phase Change Materials
SH	Space Heating
STES	Seasonal Thermal Energy Storage
TRNSYS	Simulation software for transient systems
UTES	Underground Thermal Energy Storage

Chemicals

CO_2	Carbon Dioxide
HCl	Hydrochloric Acid
Na_2CO_3	Sodium Carbonate
$NaCl$	Sodium Chloride
$NaOH$	Sodium Hydroxide

Metals according to EN

1.0036	Low Carbon Steel
1.0038	Low Carbon Steel
1.4301	Stainless Steel
1.4404	Stainless Steel
2.4060	Nickel
2.4360	Monel
2.4610	Hastelloy C4
2.4660	Alloy 20
2.4816	Inconel 600

Symbols

c [$kJ\ kg^{-1}\cdot K^{-1}$]	Specific heat capacity
$v\%$ [$m^3\cdot m^{-3}$]	Volume percent
ω [$kg\cdot kg^{-1}$]	Weight percent
ΔH [$kJ\cdot mol^{-1}$] or [$kJ\cdot kg^{-1}$]	Enthalpy
p [kPa]	Pressure
Q [W]	Heat flow
T [°C]	Temperature

1 Project Background

Switzerland aims for a 2000 W per capita society [1] by 2050 represents a drastic 63 % reduction in the current level of energy consumption. Up to date 60 % (equivalent to 3000 W per capita) of Switzerland's energy needs are met by fossil fuels, principally oil and natural gas. The building sector covers approximately 50 % of the total consumed energy, whereby a third of this is used for space heating. Key technological developments to subdue this high demand include: new types of insulation and window systems, highly efficient low temperature heating and heat recovery systems, and integrated photovoltaic and solar thermal systems. Solar thermal systems provide ideal solutions for preparing domestic hot water (DHW) in warm seasons. Work is enduring to cover the remaining heating demands with solar resources, whereby seasonal thermal storage is a key factor.

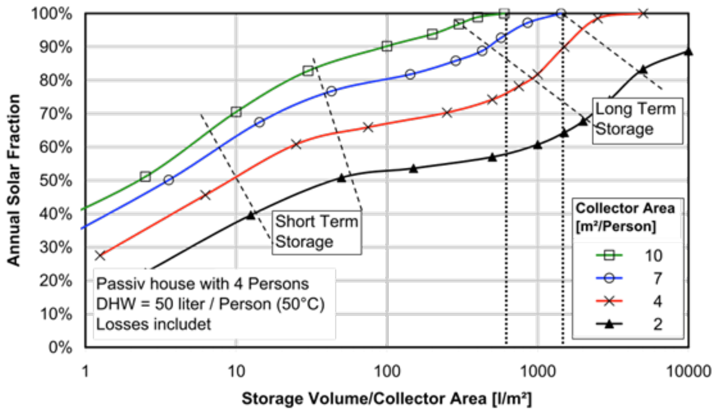
The last 40 years have seen many variations of sensible heat based Seasonal Thermal Energy Storage (STES) systems developed. Such STES systems can be accomplished in rocks, caverns, tanks and gravel beds. In a technology known as Underground Thermal Energy Storage (UTES), thermal energy sources such as energy from solar collectors, charge a subsurface store for use at a later season. In the cavern storage and pit storage, large underground water reservoirs are created in the subsoil to serve as thermal energy storage.

The use of hot water tanks is one of the best known thermal energy storage technologies and has been established on the market as an affordable solution for new low energy buildings. Using this technology, solar thermal energy is stored in large well insulated water vessels. Due to the large volume required and the constant thermal loss annual coverage is limited. Especially towards spring time storage temperatures are often not sufficient for DHW. With a substantial financial and constructive effort a sensible storage solution with coverage of 30 % to 90 % of the required thermal energy can be reached. The shortcomings of this approach though highlight the need for more research towards compact and "lossless" thermal storage. An example of a purely sensible storage solution is found in the multi apartment house in Oberburg, Switzerland. The house contains a 205 m^3 hot water storage vessel and a solar collector area of 276 m^2, supplying the house with all space heating and domestic hot water requirements.

The diagram in Fig. 1 shows the large increase in storage volume per solar collector area and person to achieve high solar fraction. Note that the storage volume is on a logarithmic scale.

In the scope of the IEA SHC Task 32, new or advanced solutions for storing thermal energy for heating or cooling buildings have been investigated and advanced technologies have been located [3]. To overcome the sensible heat storage disadvantages, Phase Change Materials (PCM) and Thermo Chemical Materials (TCM) have been investigated.

Fig. 1
Storage volume requirements in respect to solar area per person and solar fraction for sensible hot water storage.



Low temperature systems based on Thermo Chemical Materials (TCMs) function similar to chemically activated heat pumps [4]. With these technology high volumetric reductions of up to factor 7 compared to sensible thermal water storage systems are expected. In the IEA SHC Task 32 several developments were studied. All but one of the considered developments was a closed sorption systems, meaning they are closed to the atmosphere and function under airless conditions. One such system is based on the absorbent Lithium Chloride and working fluid water. This system is developed and commercialized by the Swedish company ClimateWell [5]. Due to the high material costs, the development is not suitable for seasonal storage and is mainly used for cooling other than heating. In general the development of seasonal storage systems based on chemical sorption materials appears to be complex and due to the high material costs often more suited for heat pump systems where both heating and cooling can be achieved, rather than seasonal thermal storage. This being said, there is still potential for solutions based on low cost TCMs. In addition to the high energy density compared to sensible thermal storage, the TCM system has the remarkable benefit of no thermal loss during storage.

2 Project Objectives

It is the objective of this project to develop a novel seasonal thermal storage based on the use of Sodium Hydroxide (NaOH) within a sorption process. The principle function is similar to the sorption heat pump, varying in that during the charging phase sorbent and solvent are stored for later heat gain in the discharging phase. Details to the process of a chemical heat pump are found in Appendix B.

This seasonal thermal storage should be sufficient to supply all domestic hot water and space heating requirements in a low energy house. The main advantages of this technology are high volumetric energy density and no thermal loss during storage.

The following main points were addressed in the project:

- Evaluation of the suitability of sodium hydroxide (NaOH) as a sorbent medium for thermal storage.
- Evaluation of system parameters, limitations and challenges.
- Design, construction and operation of a single stage sorption thermal storage system.
- Initial mathematical modeling of the system in MATLAB, based on lab results.
- Design, construction and operation of a double stage sorption thermal storage system.
- Assessment of system potential via dynamic simulation using the simulation program TRNSYS.
- Dimensioning of the storage volume, solar collectors and ground heat exchanger to suit a low energy house.
- System comparison in the frame of the IEA SHC Task 32.

3 Evaluation of NaOH for sorption storage

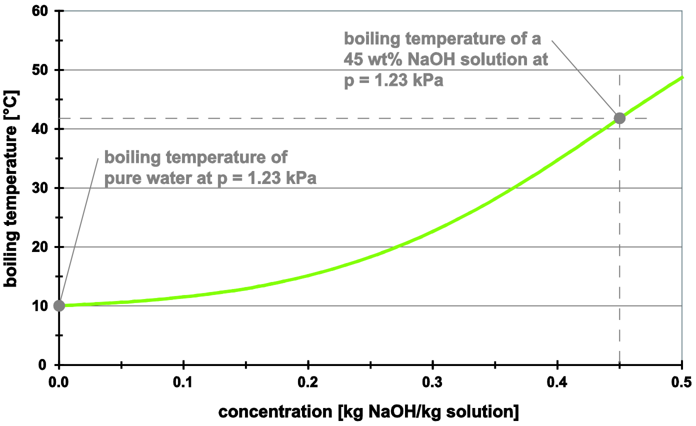
The initial literature review identified good prospects for aqueous sodium hydroxide to function well as a sorbent / solvent pair [6]. It was found that the charging and discharging temperatures occur at levels fitting to conventional solar collectors and domestic hot water requirements and that storage density is promising. For these reasons the following theoretical and practical work is based on the sorption pair sodium hydroxide and water. The picture in Fig. 2 shows the sorbent NaOH in its solid form and the working fluid water.

Fig. 2
The working pair sodium hydroxide and water as sorbent and solvent. Sodium hydroxide is shown as a solid.

In the aqueous sodium hydroxide sorption storage, diluted aqueous sodium hydroxide is heated via solar collectors on the generator / absorber whereby water is evaporated from the solution. This is similar to the concentrating process in the production of NaOH mentioned in Appendix A. The water vapor is condensed on the condenser / evaporator and both concentrated aqueous sodium hydroxide and water are stored in separate vessels. To retrieve thermal energy, the water is again evaporated on the condenser / evaporator and condensed by the concentrated aqueous sodium hydroxide on the generator / absorber. A comparison of the heat pump to the absorption heat storage can be found in Appendix B. Fig. B. 1 and Fig. B. 2 illustrate the heat pump and heat storage. In this system NaOH is the sorbent and water the working fluid.

The diagram in Fig. 3 shows the dependency of the aqueous NaOH solution concentration to boiling temperature in a water vapor atmosphere [7]. The pressure is assumed to be constant at p_{steam} 10°C = 1.23 kPa, corresponding to the water vapor saturation temperature of $T_{saturation}$ = 10 °C. Note that the increase in boiling temperature is not linear in respect to concentration.

Fig. 3
Diagram showing temperature of evaporation in respect to sorbent concentration.



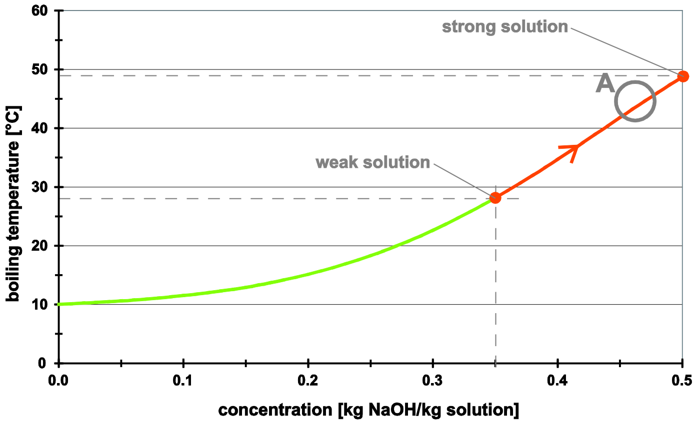
In the charging mode a diluted aqueous NaOH solution of $\omega_{weak} = 0.35\ kg\cdot kg^{-1}$ is slowly heated from $T_{weak} = 28$ °C to $T_{strong} = 49$ °C on the generator / absorber heat / mass exchanger. This process increases the concentration to $\omega_{strong} = 0.5\ kg\cdot kg^{-1}$ NaOH in the solution through evaporating part of the solvent. A constant solvent vapor pressure of p_{steam} 10°C = 1.23 kPa is achieved by condensing the generated solvent vapor on the condenser / evaporator heat / mass exchanger.

Fig. 4 shows the increase in concentration as the temperature is increased.

In this process the following can be noted:

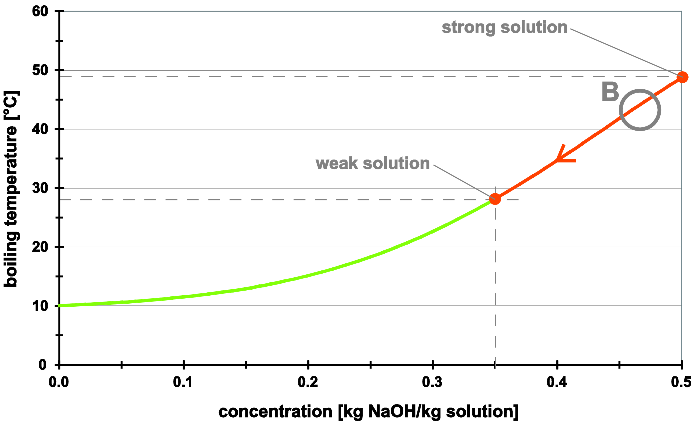
- Heating the solution from T_{weak} to T_{strong} on the generator / absorber results in the evaporation of the accordant quantity of water to increase the aqueous NaOH concentration from ω_{weak} to ω_{strong} while the steam pressure p_{steam} 10°C is kept constant by condensation on the condenser / evaporator.
- The required thermal energy to increase ω_{weak} to ω_{strong} can be approximated by the enthalpy of vaporization for water $\Delta H_{vap} = 40.65\ kJ\cdot mol^{-1}$ or $2257\ kJ\cdot kg^{-1}$ multiplied by the mass of water evaporated. The solutions specific heat capacity of approximately $c_{solution} = 3.5\ kJ\cdot kg^{-1}\cdot K^{-1}$ results only in minor deviations. Note, this thermal energy is not stored, but passed to the environment via condenser / evaporator heat / mass exchanger and ground heat exchanger.

Fig. 4
Process of charging in respect to sorbent temperature and concentration.



This process is directly reversible. The strong solution is slowly cooled on the generator / absorber heat / mass exchanger from ω_{strong} to ω_{weak} while a constant pressure p_{steam} 10°C is reached by evaporating water on the condenser / evaporator heat / mass exchanger using the low temperature input from the ground heat exchanger. Fig. 5 shows the process in respect to temperature and solution concentration.

Fig. 5
Process of charging in respect to sorbent temperature and concentration.



Again the following can be noted:

- Cooling the solution from T_{strong} to T_{weak} on the generator / absorber results in a aqueous NaOH concentration drop from ω_{strong} to ω_{weak} in as far as a constant steam supply is provided from the condenser / evaporator. The maximum temperature increase of the sorbent / solvent solution is dependent on the solution concentration and the solvent vapor pressure. The solvent vapor pressure in turn is dependent on the temperatures provided by the ground heat exchanger
- The generator / absorber accumulates the enthalpy of vaporization released on the condenser / evaporator by the evaporation of the solvent during discharge.
- Discharging results in decreasing ω_{strong} to ω_{weak} by absorption of solvent vapor.
- All statements above are valid for ideal cases with an infinite time scale for reaction .

The NaOH sorption storage is an absorption heat pump with sorbent and solvent storage. Considering the large value of the enthalpy of steam, $\Delta H_{vap} = 40.65\ kJ\cdot mol^{-1}$, water is especially suitable to be used as phase changing medium (solvent) and the high affinity of NaOH to water makes it ideal as sorbent.

The maximum achievable discharge temperature is an important factor especially for reaching domestic hot water temperatures. Required are, $T_{DHW} = 65\ °C$ and $T_{SH} = 40\ °C$. The boiling temperature of the NaOH solution is dependent on the solution concentration; this in turn defines the maximum possible discharge temperature. To reach T_{SH} the solution concentration must be $\omega \geq 0.44\ kg\ kg^{-1}$, neglecting system dependent thermal losses.

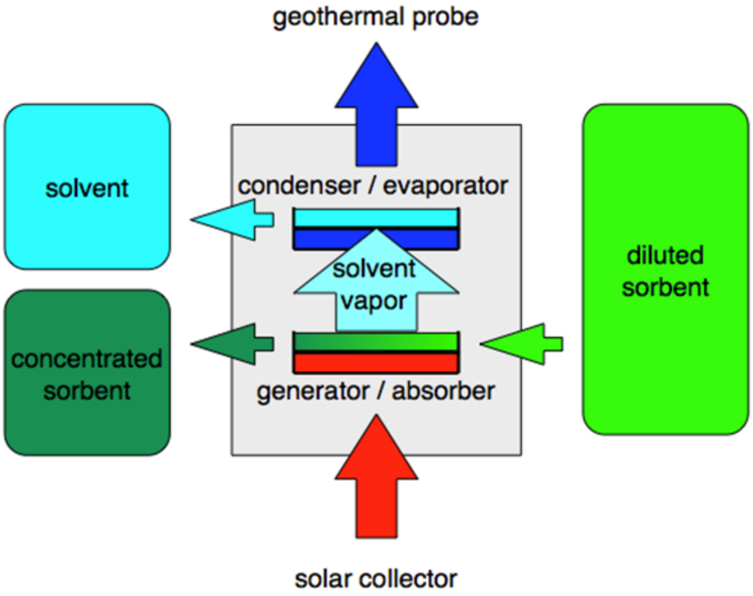
Initially both water and methanol were considered as possible solvents. Methanol has a similar enthalpy of evaporation of $\Delta Hvap = 35.28\ kJ\cdot mol^{-1}$ but one major drawback. The solution NaOH / CH_3OH solidifies at a NaOH concentration of $\omega = 0.15\ kg\cdot kg^{-1}$ at room temperature [8]. For this reason the sorbent / solvent pair NaOH / CH_3OH is not adequate for the present work. In this development it is essential that the sorbent can be pumped. The sorbent / solvent pair NaOH / H_2O solidifies at a NaOH concentration of $\omega = 0.55\ kg\cdot kg^{-1}$ at room temperature, making it more suitable.

4 System Concept

The NaOH sorption storage consists of heat / mass exchangers and storage vessels for diluted sorbent, concentrated sorbent and solvent. The generator / absorber (hot heat / mass exchanger) is in contact with varying sorbent / solvent concentrations and the condenser / evaporator (cold heat / mass exchanger) is in contact only with the solvent. The heat / mass exchangers operate as a heat pump, as described in Appendix B. They are separated from the storage vessels to enable a modular assembly, where the size and number of heat / mass exchangers defines the nominal power and the number and volume of the storage vessels defines the storage capacity.

The single stage NaOH sorption storage consists of one hot heat / mass exchanger and one cold heat / mass exchange either contained in one vessel or in separate vessels with a connection for steam mass transport.

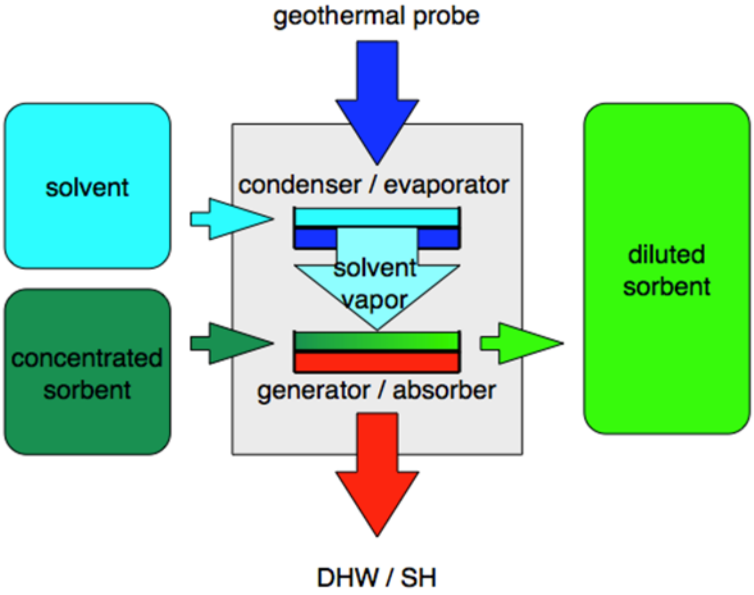
Fig. 6
Single stage NaOH sorption storage heat / mass exchangers in charging mode.



In charging mode, as seen in Fig. 6, solar heated water and diluted sorbent are introduced to the hot heat / mass exchanger, heating the diluted sorbent and evaporating some of the solvent. The cold heat / mass exchanger is cooled via ground heat exchanger, causing the vapor to condense. From the hot heat / mass exchanger the concentrated sorbent / solvent solution is stored and from the cold heat / mass exchanger the condensed solvent is stored in separate vessels. The sorbent concentration is dependent on the temperature difference between hot and cold heat / mass exchangers.

To regain heat, the process is reversed. Solvent from the storage vessel is vaporized on the cold heat / mass exchanger using low temperature thermal energy from the ground heat exchanger. On the hot heat / mass exchanger concentrated sorbent / solvent solution is introduced. The solvent vapor is absorbed by the sorbent releasing the latent heat of evaporation and increasing the temperature on the hot heat / mass exchanger in turn heating water for DHW and SH, see Fig. 7.

Fig. 7
Single stage NaOH sorption storage heat / mass exchangers in discharging mode.

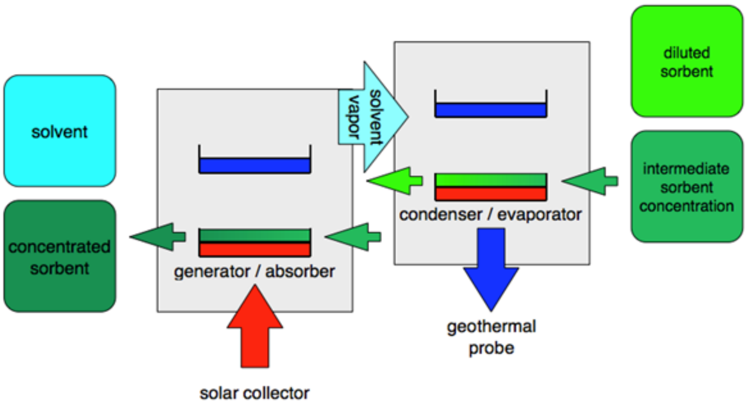


A NaOH sorption storage with two stages consists of two hot heat / mass exchangers and two cold heat / mass exchangers. The heat / mass exchangers are either pairwise, one hot and one cold, contained in vessels with the two vessels connected for vapor transport, or every heat exchanger is contained in a separate vessel and all four vessels are connected [9].

A setup with two stages allows several operating modes. The single stage function is possible with one heat / mass exchanger pair or with two in parallel. In this manner greater mass transport is possible resulting in higher charging power. These two modes can naturally also be reversed for discharging.

In addition the heat / mass exchanger pairs can operate in series. This is beneficial in charging as well as discharging when higher energy densities, for example higher temperatures, are required. If temperatures supplied are not sufficient to reach the preferred concentration, sorbent with intermediate concentration is stored in an additional vessel. This transitional sorbent concentration is introduced a second time to the hot heat / mass exchangers of both exchanger pairs. In this case one heat / mass exchanger is heated and the other is cooled. By this method the heated transitional sorbent / solvent solution is increased in concentration and the cooled transitional sorbent / solvent solution is diluted. Theoretically this method could also be achieved with just one heat pump, whereby the transitional sorbent concentration could be cooled on the cold heat exchanger. In practice this would contaminate the cold heat exchanger and cause sorbent to be introduced to the solvent storage vessel. Fig. 8 illustrates the principle of the charging double stage NaOH sorption storage.

Fig. 8
Double stage NaOH sorption storage in charging mode.



During discharging, the double stage NaOH sorption storage can supply high temperatures as required for DHW. In this mode the hot heat / mass exchangers are supplied with concentrated sorbent and the cold heat / mass exchangers with solvent in parallel. The heat / mass exchangers are switched in series so that the hot heat / mass exchanger from the first pair is directly connected to the cold heat / mass exchanger of the second pair. In this manner the solvent vapor pressure of stage two is increased which in turn increases the vapor absorption on its hot heat / mass exchanger, increasing the latent heat uptake and so the temperature. This can be a good solution to enable the supply of DHW while keeping the charged sorbent concentration below solidification at room temperature. Fig. 9 illustrates the double stage NaOH sorption storage in discharging mode. In Fig. 10 the single and double stage discharging in respect to vapor pressure is shown.

Fig. 9
Double stage NaOH sorption storage in discharging mode.

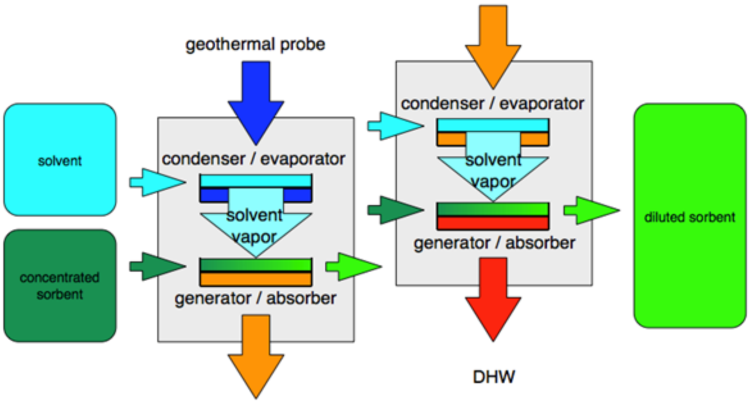
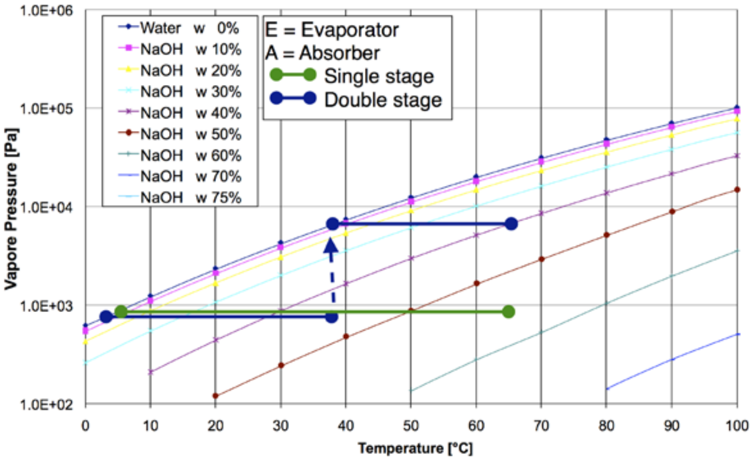


Fig. 10
Graphic illustration of the single and double stage discharging process in respect to vapor pressure, temperature and solution concentration.



4.1 Theoretical Performance

The performance of the NaOH sorption storage is best compared to the sensible thermal water storage. Initial static calculations show, the NaOH sorption storage system has the potential for volumetric reduction of a factor of 5-6 for SH and a factor of 3-4 for DHW. Fig. 11 compares various storage types in respect to their volumetric energy densities. The volumetric energy density of the NaOH sorption storage highly depends on the sorbent / solvent solution concentration, and the required raise in temperature ΔT. Fig. 12 shows the decline in energy density in respect to the temperature increase: the higher the required discharge temperature, the lower also the systems coefficient of performance (COP).

Fig. 11
Storage volume of various storage types in respect to DHW (70 °C) and SH (40 °C).

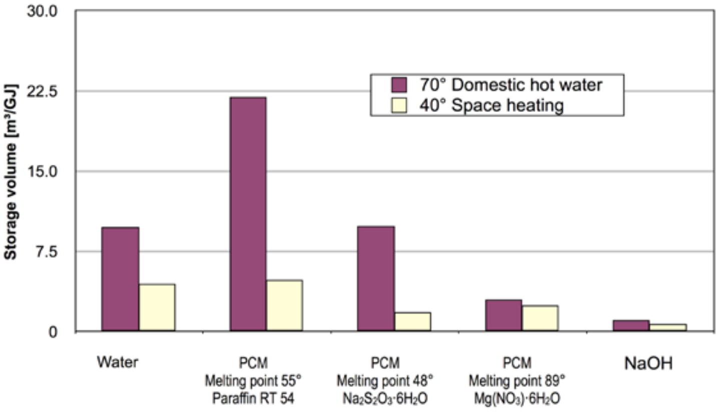
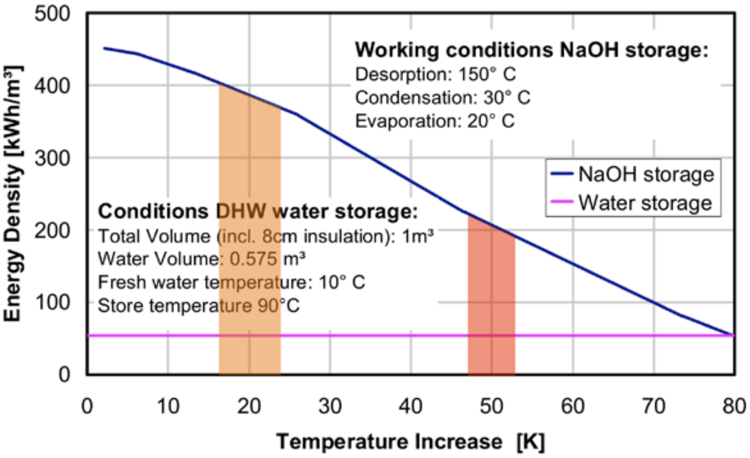


Fig. 12
Comparison of the volumetric energy density of the sensible water storage and the sodium hydroxide storage in respect to discharge temperature.



The NaOH Sorption Storage is theoretically well able to supply a low energy houses built according to Passiv-house [10] or Minergie standards with all space heating and domestic hot water requirements.

5 Laboratory Prototype

In the scope of this project a laboratory prototype was built. The idea was to get working parameters for refined TRNSYS simulations. This laboratory prototype allowed initial experience in building and operating such a system. The prototype underwent two main design steps, the primary single stage heat / mass exchanger setup, followed by the extension to a double stage version.

5.1 Single Stage NaOH Sorption Storage

Initially a single stage system was built. Fig. 13 shows the schematics of the system. Fig. 14 shows the laboratory setup. Below the crane hook, there is the heat / mass exchanger and on its left side are the storage vessels. On the right side of the heat / mass exchanger the DHW boiler is placed.

Fig. 13
Single stage NaOH sorption storage layout.

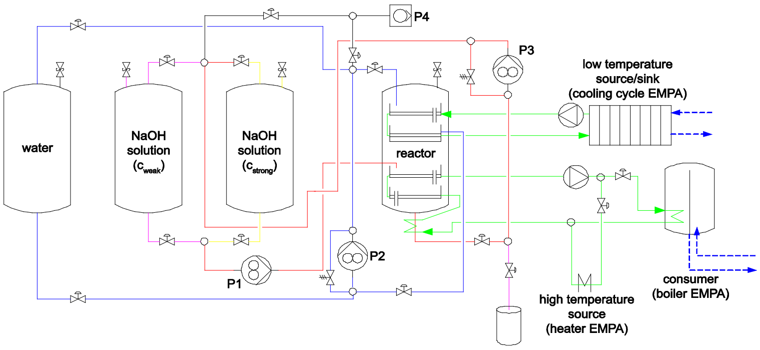


Fig. 14
Laboratory setup of the single stage NaOH sorption storage.

The prototype features a spacious design allowing for easy changes during build and operation. Wherever possible connections where welded. Otherwise vacuum components were used. The system was run with 200 liters of concentrated $\omega_{strong} = 0.5\,kg \cdot kg^{-1}$ NaOH aqueous NaOH solution.

All system components were made of stainless steel rather than nickel coated steel. In this way, corrosion was minimized while keeping maximum flexibility. Changes could easily be made; stainless steel components can be implemented and welded without requiring nickel coating. The three vessels for sorbent and solvent were built on three legged stands with a pressure sensor below one leg, to identify the quantity of fluid in the tank. The vessels have a capacity of 250 l. For safety measures, as discussed in Appendix A, the storage vessels and heat / mass exchanger vessel were placed inside a containment dyke to prevent potential solution leakage from causing greater damage. This is a necessary safety measure to take when storing aqueous NaOH solutions. As a further safety measure taken, all tanks were equipped with a rupture disc. In case, the pressure in a tank had been too high, the disc would have broken and the NaOH had been led into the dyke.

To optimize the solvent vapor transport, both the cold and the hot heat / mass exchangers were contained in one vacuum vessel, whereby the cold reactor (waterside) was placed above the hot one to prevent aqueous NaOH from contaminating the condensed water. The vapor pressure is very low, approximately $p_{charge} \approx 2.5$ kPa and $p_{discharge} \approx 0.7$ kPa. The discharging solvent vapor pressure is lower due to the low input temperature of the heat source (chilled water supply from Empa). To minimize thermal radiation from the hot heat / mass exchanger to the cold heat / mass exchanger a Polypropylene protection (blue) was placed between the heat exchangers. In addition, the same protection type (in PE, white) was wrapped around the cold heat / mass exchanger to reduce radiation exchange and solvent vapor contact with vessel walls. Fig. 15 shows two pictures of the heat / mass exchanger assembly. Due to the assumed uniform vapor flow no thermal loss from circulating vapor was expected.

Fig. 15
Initial heat / mass exchanger assembly of the hot and cold exchangers in one vessel. The right picture shows the insulation measures taken.

Being a lab setup the solar heat source was simulated using an electric continuous flow heater and the ground heat exchanger was replaced with the institute's chilled water supply. The system was controlled and monitored via a LabVIEW® program.

For ease of handling and reliability all liquids are pumped, thus crystallization of the concentrated sorbent must be prevented. Stainless steel gear pumps with magnetic drive were used to pump all mediums in the airless atmosphere. As can be seen from Appendix A this is an appropriate measure to minimize aqueous NaOH corrosion on pumps as well as reducing vacuum leakage potential. Because of the minute suction effect produced by pumps in a vacuum environment they were placed at the lowest point in the plant setup to benefit from gravity driven flow. Concentrated aqueous sodium hydroxide has a very high viscosity (as honey) compared to water which leads to accordingly high head losses when pumped. Consequently, transport of concentrated lye was insufficient in the test setup. By mounting the pump directly below the vessel containing concentrated NaOH and thus minimizing the transport distance the problem finally could be overcome (Fig. 16).

Pipes of stainless steel were used. The pipes were connected to vessels, valves and pumps with vacuum flanges, which were welded to the tubes. This was done to remain flexible. In a final product, as much as possible should be welded directly. Stainless steel is an appropriate material to be used in contact with aqueous NaOH solutions, for cost optimizations nickel coated steel can be used. The sealing rings for these connections proved to be hazardous. Viton® O-rings were used. Experience showed that when mounted the first time, these were tight, but if dismounted after being in contact with hot aqueous NaOH solution, they were slightly damaged and had to be replaced. To solve this problem the Viton® O-rings were replaced with Polytetrafluoroethylene (PTFE, Teflon®) rings. These in turn were mechanically not stable enough at the given temperatures and were only tight for a short time. With no other options, available Viton® O-rings were used again. Fig. 17 shows the various sealing rings.

Fig. 16
The pump was installed directly beneath the heat exchanger containment to reduce pipe length. Also clearly to see: the electrical trace heating to prevent crystallization. (Picture without insulation)

Fig. 17
Various sealing rings tested. On the left two Viton® O-rings and on the right PTFE.

Sealing in general proved to be more demanding than initially assumed. Considerable care had to be taken to bend and fit the tubes well. In the end it was found that the purchased stainless steel vacuum valves were the main cause of leakage. It seems that the valve sealing mechanism was corroded by the aqueous sodium hydroxide.

Inside the heat / mass exchanger assembly silicon tubes were used to allow flexible connection between the heat exchanger dishes. Product sheets showed that silicon is resistant to aqueous sodium hydroxide. What was not taken in consideration was the steam atmosphere present during operation. The combination of vapor and NaOH let the silicon deteriorate rapidly, see Fig. 18, and they had to be replaced with more stable tubes made of Teflon®. These proved to be too stiff, preventing adequate sealing. In the end Viton® tubes were found to be the solution.

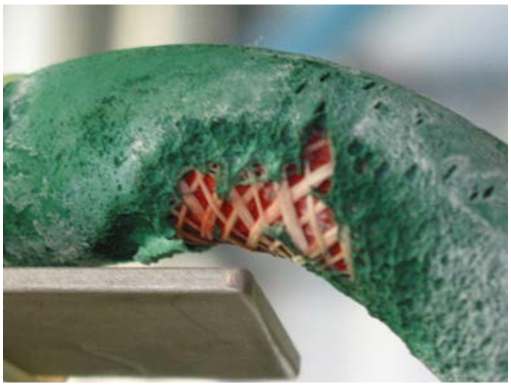


Fig. 18
Picture of the corroded silicon tube after 10 hours of operation.

In general it was found that system heat losses were very high. This reduced the efficiency markedly and more severely caused crystallization in the pipes, which clogged them completely. The only way to remove the crystals was to dismount the pipes and introduce fresh water to dissolve the NaOH crystals. This always proved to be a process of several days till the system could operate again. To prevent crystallization all critical pipes and vessels were insulated and actively heated. In a next design this naturally has to be solved otherwise, electric heating of pipes and vessels cannot be the solution.

The heat / mass exchangers were designed as plates with a double bottom to contain the hot or cold water. Aqueous sodium hydroxide is introduced on top of the hot plate to evaporate part of the water. This construction functions, but is very sensitive to pressure due to the large unsupported surface areas. It is important that the surface where the aqueous NaOH rests is leveled. Otherwise the aqueous NaOH will not cover the whole plate and so the area of reaction will be reduced. For the second heat / mass exchanger pair the heat / mass exchanger plates were equipped with guides for the aqueous NaOH so that bypassing of diluted aqueous NaOH could be prevented as illustrated in Fig. 19.

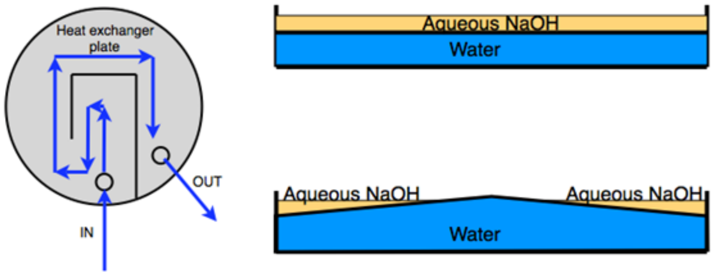


Fig. 19
The left illustration shows the flow of the aqueous NaOH solution. The right picture illustrates the problem caused by high water pressures.

For testing purposes and analysis of the behaviors in the heat / mass exchanger vessel a view into the vessel is assistive. Due to the corrosive behavior of aqueous NaOH on glass a thin transparent Teflon® foil was placed in front of the viewing glass as a protective film.

Placing both generator / absorber and condenser / evaporator in the same vessel was found to cause high direct thermal transport between the two heat / mass exchangers via radiation and steam circulation. For this reason the second heat / mass exchanger pair for the extension to two stages was designed so that two separate vessels contained the exchangers and the vessels were connected via pipe with large inner diameter to reduce flow resistance.

5.2 Double Stage NaOH Sorption Storage

Due to the low discharging temperatures achieved, it was decided to extend the laboratory setup to include a second heat / mass exchanger pair. To prevent the high thermal loss encountered in the initial setup, the second heat / mass exchanger pair was designed to have generator / absorber and condenser / evaporator heat / mass exchangers incorporated in two separate vessels. Fig. 20 illustrates the varying setup and Fig. 21 shows the generator / absorber of the second stage.

Fig. 20
Illustrated difference between the single vessel heat / mass exchanger assembly and the dual vessel version.

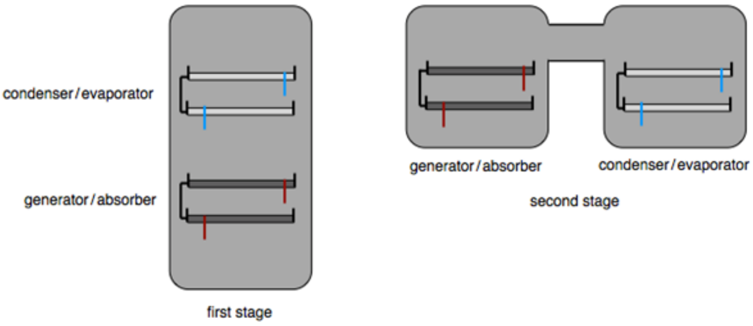


Fig. 21
Picture of the second stage generator / absorber.

In addition to the second heat / mass exchanger pair a further vessel to store the high concentrated sorbent / solvent solution was added. This tank is heated and will allow concentrations of up to $\omega \geq 0.75\,\mathrm{kg \cdot kg^{-1}}$. Fig. 22 shows the setup of the second heat / mass exchanger pair. The two individual heat / mass exchanger vessels are placed above the insulated and heated high concentration vessel.

Fig. 22
Picture of the laboratory prototype with the second heat pump and the additional high concentration storage vessel.

5.3 Measurement setup

The measurement setup can be seen in Fig. 23. The data acquisition and control functions were done on a PC with an in-house developed LabVIEW program. In vessel 4 (heat and mass exchanger) not all sensors are indicated. For more detailed information see also Fig. 25.

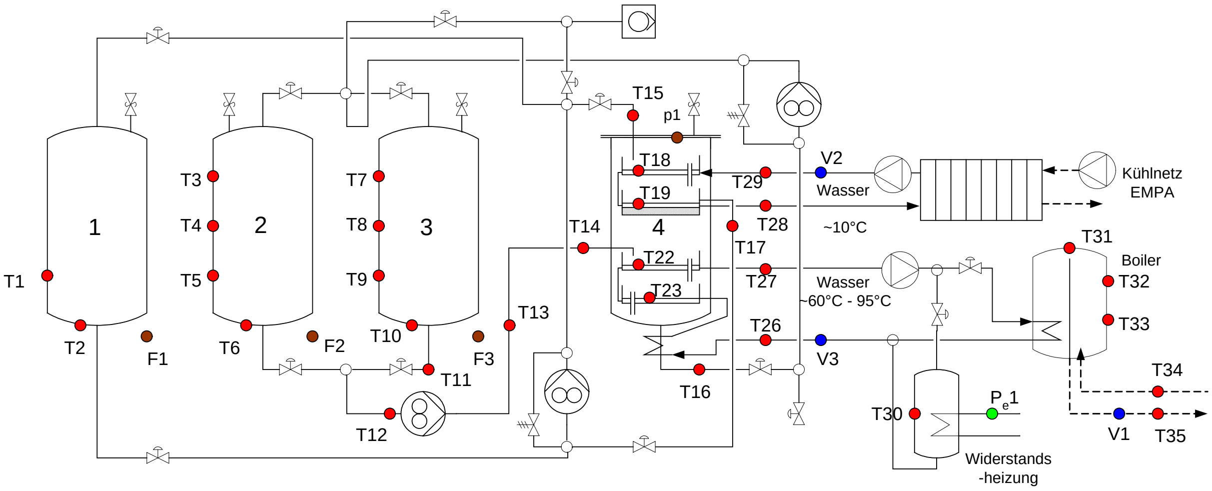


Fig. 23 Measurement setup for the single stage setup

The signals from the different sensors were measured mainly by two devices:

1. HP 34790 Data Acquisition unit equipped with
    - 2x Agilent 34901A, 20 Channel Multiplexer
    - 1x Agilent 34907A, Multifunction Module
2. IOtech Daqboard 2000

The IOtech Daqboard 2000 also allowed for digital output (DIO). This DIO was used to actuate relays and to operate the whole system.

Table 1 Sensors used

Sensor No.	**Physical value**	**Type**	**Precision**	**Measured by**
T1 – T25	Temperature	TC Type T	± 0.15K (*)	HP 34790
T26 – T35	Temperature	RTD PT100	± 0.10K (**)	HP 34790
P1	Absolut pressure	Vacubrand DVR5 (***)	± 1 mbar	RS 232 to PC
V1&V2	Mass flow water	GWF Unico Impuls	± 3%	Daqboard 2000
V3	Mass flow water	FCH midi PVDF Turbine	± 2%	Daqboard 2000
F1 – F3	Force (weight)	LD1.200kg.A1	± 0.2%	HP 34790
Pe1	Power	Finder 7E, 3-phase	± 3%	Daqboard 2000

(*) measured with an external temperature reference
(**) T26&27, T28&29, T34&35 were pairwise calibrated
(***) Sensor with absolute values, independent gas type, chemically resistant

There is no device for the direct measuring of the lye concentration. The concentration was evaluated by the temperature of the lye and its vapor pressure by using according relations [11]. This method delivers exact results are only in case of boiling lye or if an equilibrium state is possible.

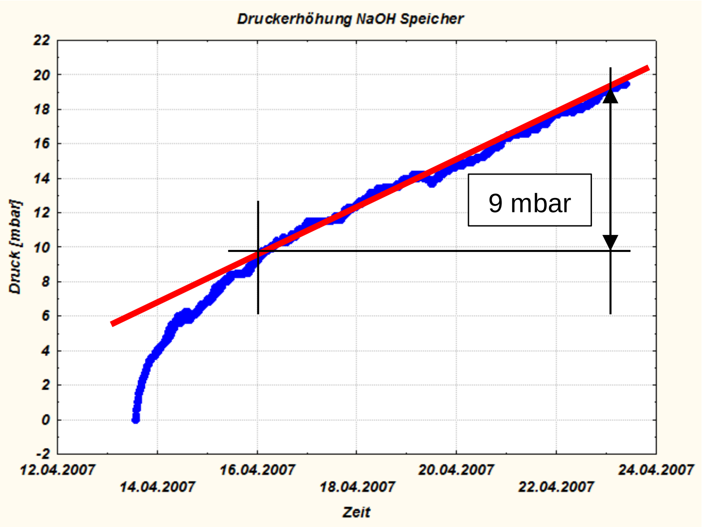
5.4 Testing and operation

Before the system was filled with NaOH for the first time, all measurement devices and gear pumps were calibrated using deionized water. It was seen that during operation, the pumped volume in the pumps fluctuated because of the changing viscosity. Nevertheless, the weight measurement from the tanks allowed recalibrating the pumps.

After first tests, it was learned that the lye and the water inside the system need to be degasified, because of problems with inert gases hindering the process of water vapour absorption.

Prior to commissioning, air was consequently removed from the complete system using a vacuum pump. The system was only opened for maintenance purposes. In the case that the system was opened for maintenance or changes where undertaken, vacuum tightness had to be reconfirmed. This was a time consuming task. As the system was already filled with aqueous NaOH, it was not possible to evacuate the system completely, due to the presence of water vapor influencing the pressure. In order to assess gas tightness, stable pressure had to be verified over several days. Experiments could be continued if the average increase over the last seven days was smaller than 2 mbar (in Fig. 24, there was an increase of 9 mbar).

Fig. 24
With time-pressure curves, the tightness of the system was evaluated. In this case, the system was not tight enough to perform experiments.



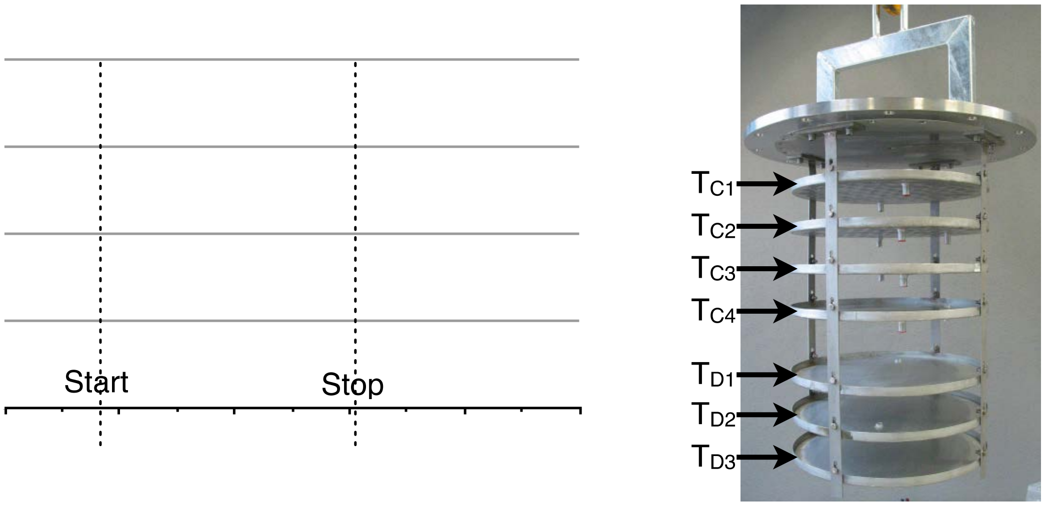


Fig. 25 Measured sequence from a desorption test. The temperatures T_{Cx} are on the condenser side, whereas the T_{Dx} on the desorption side are.

For charging of the storage, desorption conditions in the heat exchanger had to be reached first. As shown in Fig. 25, there is a pre-charging time in the range of 1 to 2 hours prior to operation. In that time, neither lye nor water was introduced onto the plate heat exchanger. When reaching stable temperature conditions, diluted lye was pumped.

In charging mode good results were achieved. With a generator temperature of 95 °C and a condenser temperature of 12 °C aqueous NaOH concentrations of $\omega = 0.62\ \mathrm{kg \cdot kg^{-1}}$ to $\omega = 0.65\ \mathrm{kg \cdot kg^{-1}}$ were reached, with a maximum efficiency of approximately 80 %. The charging power was between 2 kW and 3 kW. Both, concentration and efficiency were measured indirectly. The concentration of the lye was determined by measuring the pressure inside the containment and the lye temperature on the lowest plate of the heat exchanger (T_{D3} in Fig. 25.). With a pressure-temperature-concentration diagram, the concentration could be determined. The efficiency was gained by measuring the mass flows, the heating power (from the electrical heater) and the inlet and outlet temperatures of the lye and water. The efficiency was strongly dependent on the temperature of the whole mass/heat exchanger. Start efficiency was in the range of 40%, after 5 hours of charging, 80% could be reached.

The discharging process proved to be unstable. Discharging with the $\omega = 0.62\ \mathrm{kg \cdot kg^{-1}}$ to $\omega = 0.65\ \mathrm{kg \cdot kg^{-1}}$ concentration was not possible.

Prior to the development and actual testing of the NaOH storage experts from industry were interviewed for their experience. Together, security issues, technical limitations, corrosion issues and material issues were discussed. One of the most important statements was about pumping NaOH with high concentration > 50% at low temperature. The statement was, pumping is possible but like pumping ice slurry. Pumping this slurry with gear pumps was also said possible. During first testing it was though discovered that this was not possible in our case. The very small mass flow in our setup, made it impossible to handle high concentrations as initially assumed. As soon as there was a cold spot in the tubing, crystallization took place. The flange of the Reactor had a thickness of 30 mm. The feed-through in this flange couldn’t be heated and with the low Mass flow ($\approx 0.1\ \mathrm{kg \cdot Min^{-1}}$) of NaOH solution, the tube was blocked with crystals within 10 – 15 minutes making it impossible to pump the solution.

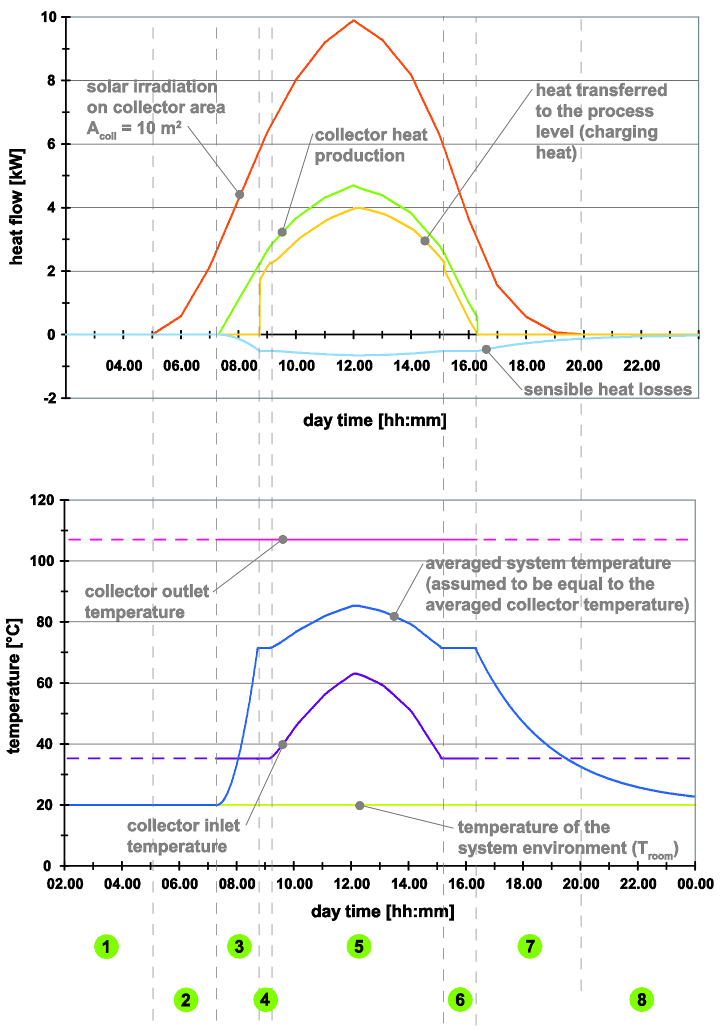
6 Simulation

For this project, two types of simulations were carried out. The first simulation was based on MATLAB to estimate the theoretical performance of a NaOH-storage system. The second was based on TRNSYS with the goal of simulating the test building for IEA task 32.

6.1 Theoretical performance simulation of NaOH storage

The aim of this simulation was the calculation of the performance and the evaluation of the application potential of NaOH storage for building heat supply systems [12]. This simulation was done before the prototype went into operation with the goal to learn lessons from the simulation before the experimental work starts. The following tasks were defined as part of the simulation:

- To develop a model of a NaOH accumulator and implement it into MATLAB.
- To specify and model an application of the NaOH accumulator for a building heat supply system.
- To evaluate and assess such a system in terms of energy and (as far as possible) to perform optimizations.



① No solar heat input. The system temperature is at the lowest level (night phase).

② Solar input is to low, collector cycle cannot yet be switched on ($\eta_{coll} < 0$).

③ Collector cycle is switched on, heat production starts. The system temperature (and simultaneously the sensible heat losses) increases until the required operating temperature to switch on the solution cycle is reached.

④ The solution cycle is switched on, heat can be transferred to the process level. The system temperature can be kept constant since the solar input is not too high (no heat transfer limitation in the solution heat exchanger).

⑤ The solar input increases further on, the produced heat can not be transferred completely to the process level. Therefore, the collector inlet temperature (and the system temperature) increases. The collector efficiency is decreasing and the sensible heat losses are slightly increasing due to the elevated system temperature.

⑥ Again, all the heat produced can be transferred to the process level. The system temperature stays constant.

⑦ No more heat can be transferred to the process level. The solution cycle and the collector cycle are switched off and the system cools down by sensible heat losses.

⑧ Solar heat input goes down and the night phase begins.

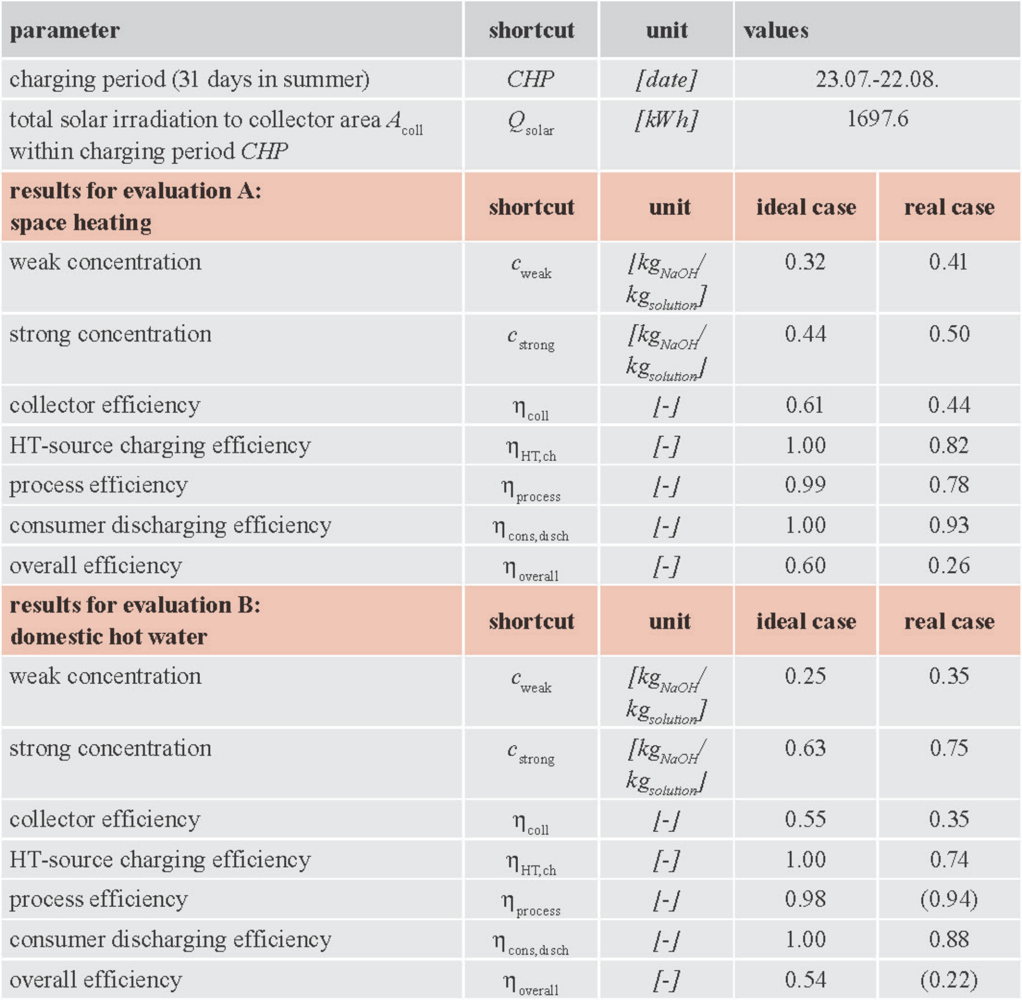
Fig. 26 Operating temperature and heat flows from 22nd of August (DRY-year Kloten)

A MATLAB simulation was implemented (see also Appendix C). With this simulation, a maximum of a 31 day simulation time was covered. The MATLAB model used a flexible time step to solve the simulation task. This led to very high computational costs. A one-month simulation needed more than two days to complete. In Fig. 26 a typical simulated day is shown.

The simulation was done for one month in summer and one month in winter. Heating load and load for domestic hot water in winter was assumed to be constant. This was realized by using a buffer between the sorption storage and the consumer. The deliveries for heat and DHW were handled in separate simulations.

The “ideal case” in this simulation describes the situation, when no heat losses occur, temperature differences in additional heat exchangers are negligible, and all chemical reactions take place entirely. The real case considers those issues and associated limitations/losses. The simulation was done with one sorption stage; double stage sorption was not considered.

Table 2   Summary of the simulation results



parameter	**shortcut**	**unit**	**values**	
charging period (31 days in summer)	*CHP*	*[date]*	23.07.-22.08.	
total solar irradiation to collector area A_{coll} within charging period *CHP*	Q_{solar}	*[kWh]*	1697.6	
results for evaluation A: space heating	**shortcut**	**unit**	**ideal case**	**real case**
weak concentration	c_{weak}	$[kg_{NaOH}/kg_{solution}]$	0.32	0.41
strong concentration	c_{strong}	$[kg_{NaOH}/kg_{solution}]$	0.44	0.50
collector efficiency	η_{coll}	*[-]*	0.61	0.44
HT-source charging efficiency	$\eta_{\text{HT,ch}}$	*[-]*	1.00	0.82
process efficiency	η_{process}	*[-]*	0.99	0.78
consumer discharging efficiency	$\eta_{\text{cons,disch}}$	*[-]*	1.00	0.93
overall efficiency	η_{overall}	*[-]*	0.60	0.26
results for evaluation B: domestic hot water	**shortcut**	**unit**	**ideal case**	**real case**
weak concentration	c_{weak}	$[kg_{NaOH}/kg_{solution}]$	0.25	0.35
strong concentration	c_{strong}	$[kg_{NaOH}/kg_{solution}]$	0.63	0.75
collector efficiency	η_{coll}	*[-]*	0.55	0.35
HT-source charging efficiency	$\eta_{\text{HT,ch}}$	*[-]*	1.00	0.74
process efficiency	η_{process}	*[-]*	0.98	(0.94)
consumer discharging efficiency	$\eta_{\text{cons,disch}}$	*[-]*	1.00	0.88
overall efficiency	η_{overall}	*[-]*	0.54	(0.22)

In Table 2, the resulting efficiencies are shown. The expected concentration of the diluted lye (weak concentration) shows the storage capacity; the lower the concentration, the higher the specific heat density. The strong concentration is the minimum concentration needed to operate one stage absorption.

The overall efficiency in table includes the whole chain of efficiencies form solar collector to the end user. The separate efficiencies are divided in collector, charging, process and discharging efficiency where process stands for sorption storage (see equations below). In the ideal cases, some of those efficiencies are close to one with the meaning: there are no losses. In the real case and for space heating, the value for the sorption storage shows 78%. This is a quite ambitious value and indicates that there are still not all losses included. The real case value for domestic hot water (process efficiency) is extremely high an indicated in brackets. During simulations, phase change occurred and falsified the result.

$$\eta_{\mathrm{coll}} = \frac{Q_{\mathrm{coll}}}{Q_{\mathrm{solar}}} \quad \textit{collector efficiency}$$

$$\eta_{\mathrm{HT,ch}} = \frac{Q_{\mathrm{charging}}}{Q_{\mathrm{coll}}} \quad \textit{HT-source charging efficiency}$$

$$\eta_{\mathrm{process}} = \frac{Q_{\mathrm{discharging}}}{Q_{\mathrm{charging}}} \quad \textit{process efficiency}$$

$$\eta_{\mathrm{cons,disch}} = \frac{Q_{\mathrm{useful}}}{Q_{\mathrm{discharging}}} \quad \textit{consumer discharging efficiency}$$

$$\eta_{\mathrm{overall}} = \eta_{\mathrm{coll}}\, \eta_{\mathrm{HT,ch}}\, \eta_{\mathrm{cons,disch}} = \frac{Q_{\mathrm{useful}}}{Q_{\mathrm{solar}}} \quad \textit{overall efficiency}$$

From this simulation was learned, that crystallization might be a problem. Together with security issues, this was the reason to contact industrial experts and to seek technical advice (see also chap. 5.4).

6.2 Building simulation integrating NaOH storage

The TRNSYS simulation has the aim to reproduce the prototype as mathematic model and to compare systems for the IEA SHC Task32 test building [13]. The idea of the Types programmed is described in Appendix D.

The first simulation was done with MATLAB (Chapt. 6.1) and had some shortcomings:

- The whole simulation had only one stage and was only able to simulate correctly with high concentration of the lye to come to results.
- It was not possible to run a yearly simulation
- It was derived from physical and chemical relations, real life issues (as heat losses, pumping issues, internal losses, kinetics) were not considered
- The building was not adequately modelled
- There was no parallel operation of solar production and heat production by the storage (meaningful in spring and fall)

With the TRNSYS simulation, it was the goal to overcome those issues. Unfortunately, this simulation was never brought to a numerically stable version and did hence not yield valid results. Major reasons for the problems encountered were caused by the fact that the operation conditions are close to the borderline of liquid to solidification. At this borderline, some of the physical parameter change drastically. Unfortunately, those changes lead to unstable numerical situations during the iteration process. This issue is valid for the evaporation enthalpy, the internal energy, and the concentration-temperature-vapor pressure relation. The latter was anyway only defined in the liquid phase; no measured data is available for the solid phase. Despite of tailored iteration schemes no convergence could be achieved.

Therefore simulations for the SHC Task 32 to compare the NaOH storage with other storage systems never took place.

7 Conclusions and Outlook

To cover the required thermal energy for domestic hot water and space heating from solar energy seasonal storage is crucial. The NaOH sorption storage is a promising solution due to its high volumetric energy density and negligible loss during storage. In this project a storage prototype using the sorption pair sodium hydroxide and water was developed built and tested.

Charging test with one stage showed, that with a condenser inlet temperature of about 10° ± 2°C and a generator inlet temperature of 95 ± 3°C a concentration increase to $\omega = 62 – 65\%$ $kg \cdot kg^{-1}$ was possible. With a heating power of 3kW the efficiency was in the range of 80%. Unfortunately, the absorption never worked sufficiently, such that valid results from measurements are not available. The main reason was crystallization in the tubing, especially in the feed-through of the housing.

The preliminary performance simulation with MATLAB showed efficiencies within the expected range, whereas the TRNSYS simulation was numerically instable and did not produce meaningful results.

There was no notable corrosion on the stainless steel vessels or other stainless steel components during the experimental time. However, a few weeks after dismantling the system, the color of the stainless steel which was for a long time in diect contact to NaOH, turned to black. We assume that in the tanks (without oxygen) the corrosion was not visible. But as soon as the parts get into contact with air, corrosion starts. This mechanism is unclear and has to be verified. From literature study, the grade 1.4404 (SAE316) stainless steel was concluded to be adequate (Fig. 27). For a next prototype though nickel coated steel would be used for many components to reduce high material costs and corrosion issues. In addition, the quantity of material, in terms of material thickness, would be reduced.

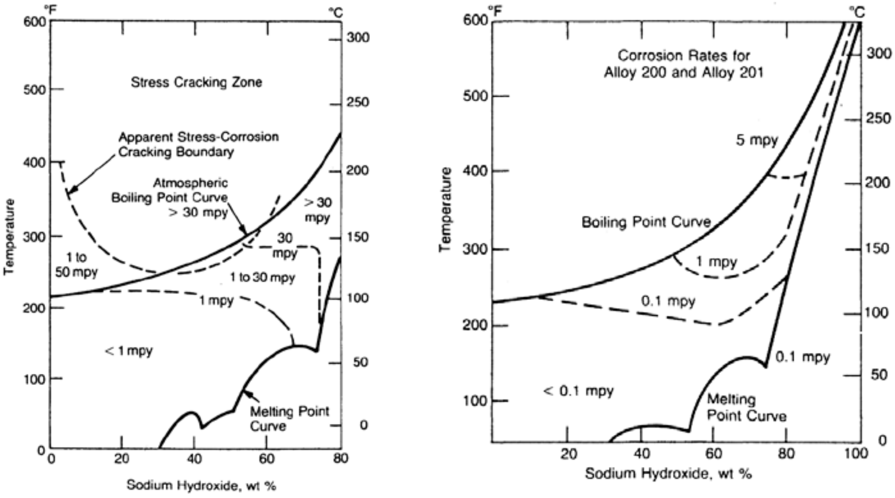


Fig. 27
Left diagram shows corrosion of stainless steel 304 and 316, the right diagram the corrosion of Nickel 200. [14]

Working with NaOH proved not to be a problem as long as the necessary precautions were met (see Fig. 28). Whenever work was done on the open system or pipes were unclogged, chemical suits, face shields rubber gloves and robber boots were worn.

Water used to wash NaOH contaminated components was neutralized using hydrochloric acid, and then disposed of in the canalization. See Appendix A for further details.

Shelf life reduction due to carbonation was no problem in the setup. Due to the system operating under airless conditions the aqueous NaOH will have a long operating time. The condensed solvent showed no noticeable trace of sorbent, it can be concluded that the vapor transport between the heat / mass exchangers is pure solvent. This gives good prospects for achieving high conversion efficiencies.

Fig. 28
The picture shows the first heat / mass exchanger pair being cleaned.

Further work regarding NaOH storage will focus on optimizations of mass-heat exchangers, reduction of component cost and system volume and over-all increase of performance. This will lead to a second generation prototype, hopefully ready for field testing.

8 References

[1] IEA SHC Task 32 - Advanced Storage Concepts for Solar and Low Energy Buildings, July 1, 2003 to December 31, 2007

[2] Koschenz M, Pfeiffer A, Wokaun A. Energy and building technology for the 2000 W soci-ety - Potential of residential buildings in Switzerland. Energy and Buildings 2005; 37: 1158–1174

[3] Hadorn J C et al. Thermal energy storage for solar and low energy buildings - State of the art. IEA SHC Task 32, 2005. ISBN: 84-8409-877-X. www.iea-shc.org >Task 32

[4] K. Edem N'Tsoukpoe et al., A review on long-term sorption solar energy storage, Renewable and Sustainable Energy Reviews, 13 (2009) 2385–2396.

[5] Bales C, Setterwall F, Bolin G. Development of the Thermo Chemical Accumulator (TCA). Proc. Eurosun 2004, Freiburg, Germany

[6] Mugnier D, Goetz V. Energy storage comparison of sorption systems for cooling and refrigeration. Solar Energy 2001; 71/1: 47-55

[7] Zaytsev I, Aseyev G. Properties of aqueous solutions of electrolytes. CRC Press 1992; ISBN: 0-8493-9314-0

[8] Gmehlin Handbook of Inorganic Chemistry. Na. Natrium. Sodium (System-No. 21) 8. Ed. 4th Volume, and System-No. 21, 8. Ed. Main volume. Springer

[9] Weber R., Dorer V., Long-term heat storage with NaOH. Vacuum 82, 708-716.

[10] Feist W. The Passivhaus Standard - requirements for quality approved Passive Houses, Passivhaus Institut, Darmstadt, 2002 (In German).

[11] J. Olsson, A. Jernqvist, G. Aly, Thermophysical properties of aqueous NaOH-H2O solu-tions at high concentrations, International Journal of Thermophysics, Vol. 18, No.3, 1997 (Springer).

[12] Sigrist D., NaOH heat storage: performance and application potential, Master thesis, 2006 Dübendorf

[13] Luccini G., Long term heat storage using NaOH solutions, Master Thesis, Dübendorf 2010

[14] McKetta J. Encyclopedia of chemical processing and design. NewYork (Basel): Marcel Dekker Inc.; 1976.

[15] Caustic Soda - SOLVAY Technical and Engineering Service, Bulletin N° 6 (1967)

[16] Alefeld G, Radermacher R. Heat conversion systems. CRC Press 1994; ISBN 0-8493-8928-3

[17] ASHRAE Research, “ASHRAE Handbook-Fundamentals.SI Edition”, 2009

Appendix A Aqueous Sodium Hydroxide

Sodium hydroxide (NaOH), also known as caustic soda, is a colorless odorless solid. It is non occurring in nature but industrially produced on a large scale for a diversity of appliances. According to Ullmann's Encyclopedia of Industrial Chemistry production in 2004 is estimated at 60 million tones. The following is a sum up of information on sodium hydroxide applicable to the project. The information originates from Solvay Chemicals International SA, Europe and Occidental Chemical Corporation, USA as well as Ullmann's encyclopedia of industrial chemistry.

A1. General Information

Manufacturing Process

Aqueous sodium hydroxide is produced commercially by an electrolytic process. Brine, prepared from sodium chloride and water, is electrolyzed in either a mercury cell, diaphragm cell or membrane cell. The coproducts are chlorine and hydrogen.

In the mercury cell process, a sodium-mercury amalgam is formed in the cell. The amalgam is sent to a decomposer where it is reacted with water to form aqueous NaOH, hydrogen and free mercury. The free mercury is returned to the electrolytic cell. The resulting water diluted NaOH solution has a concentration of 50 %. This method is the least efficient in respect to electric energy required for production.

In the membrane process, the anode chamber is fed with purified and concentrated aqueous sodium chloride solution. This is decomposed electrolytically to chlorine at the anode of the cell and sodium ions migrate to the cathode chamber through the membrane. Depleted brine exits the anode chamber. The cathode chamber is fed simultaneously with diluted aqueous NaOH. Water is decomposed electrolytically to hydrogen at the cathode of the cell and hydroxide ions are combined with sodium ions. Concentrated aqueous sodium hydroxide exits the cathode chamber. A solution of approximately 30 % in strength is formed. The solution is then sent to evaporators, which concentrate it to a strength of 50 % by removing the appropriate amount of water.

The diaphragm process is very similar to the membrane process except that a solution of only 10 % to 12 % is formed in the cell. Therefore, additional evaporation is required to reach the concentration of 50%.

The purity of the aqueous NaOH solution is dependent on the production method. Major impurities in the solution include, sodium carbonate, sodium sulphate, sodium chlorate, potassium and heavy metals such as iron and nickel. The mercury cell process produces the most pure aqueous NaOH solution containing 20 ppm to 30 ppm of chloride (Cl-). The diaphragm cell production on the other hand, yields aqueous NaOH with up to 1 w% of sodium chloride (6'000 ppm Cl^-). Impurities in the aqueous NaOH solution can cause stress corrosion cracking.

The anhydrous forms of NaOH are obtained through further concentration of 50% NaOH. Solid NaOH results when molten NaOH, from which all the water has been evaporated, is allowed to cool and solidify. Flake NaOH is made by passing molten NaOH over cooled flaking rolls to form flakes of uniform thickness. The flakes can be milled and screened into several crystalline products with controlled particle size. The manufacture of NaOH beads involves feeding molten liquor into a pilling tower under carefully controlled operating conditions, producing a spherical bead.

Methods of Shipping

Aqueous sodium hydroxide is available as a 50% solution and anhydrous sodium hydroxide is generally supplied in four forms; beads, flakes, compounders and solid castings. Large quantities are transported by tank truck, tank car, barge or ship. Smaller quantities are contained in a combination package, consisting of inner packs of polyethylene bottles and a strong outer pack of plywood, fiberboard or plastic box. It is further recommended to envelop the bottles with a plastic bag. The inner pack must be secured or cushioned in such a way that it cannot break during normal conditions of transport.

Storage

Aqueous sodium hydroxide must be stored in compliance with relevant federal laws and regulations. The storage tank should be labelled with the product name and safety symbol. Aqueous sodium hydroxide is a corrosive product. It is currently stored in steel, nickel, nickel alloys or certain types of plastic materials. The choice is determined by temperature, concentration, tank location, safety issues and the end use. If there is a risk of solidification due to the product freezing at low temperatures, a temperature controller should be installed. The storage tank must be mounted on an adequate reinforced concrete foundation to support the tank and must be placed in a bund, containment dyke or be double walled. Aqueous sodium hydroxide corrodes concrete. An epoxy paint coating gives good corrosion protection.

Application

Sodium hydroxide is one of the very few chemicals finding a very broad range of applications. The largest users of sodium hydroxide are the pulp and paper, detergent and chemical industries. Further it is also used in the alumina, oil and gas and textile industries, mostly for its alkalinity value.

Environmental Contamination Concerns

Sodium hydroxide is a hazardous substance. Discarding sodium hydroxide or sodium hydroxide solutions into the canalization will raise the pH value. This can have severe consequences to living organism in contact. Sodium hydroxide is highly reactive and is rapidly neutralized by organic chemicals in soil. For this reason soil contamination is not critical, and sodium hydroxide is not expected to migrate downward through soil to groundwater. Sodium hydroxide is subject to wet deposition (washout by rainfall) and dry deposition. It will readily combine with water vapor in air, and the resulting aerosol or mist will be corrosive. In general it can be said that sodium hydroxide readily reacts with organic materials whereby it is neutralized.

Recycling

Aqueous sodium hydroxide can be recycled and purified by means of electrolysis, filtration and evaporation. In many cases the effort if recycling is markably less then that of the initial production.

Disposal

Aqueous sodium hydroxide must be disposed of in compliance with relevant laws and regulations. Large quantities are to be returned to the supplier or disposed of via chemical disposal company. Small quantities can be neutralized using hydrochloric acid (HCl) to produce water and sodium chloride (NaCl). This salty water can then be disposed of in the canalization. Contaminated rags, bottles, etc can be disposed of in the normal domestic wast. Care should be taken that such wastes are disposed in plastic bags, to prevent human contact as well as contact with possible corrosive material.

Pricing

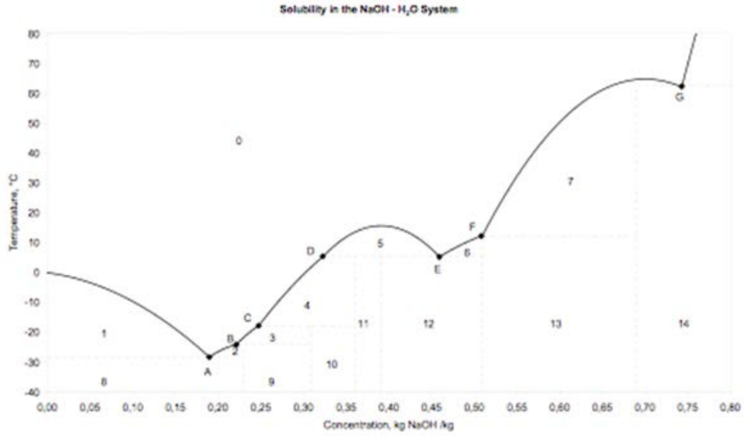
NaOH is widely used and industrially produced on a large scale. The price of NaOH is largely dependent on delivery quantity and vessel type as well as handling and transport efforts.

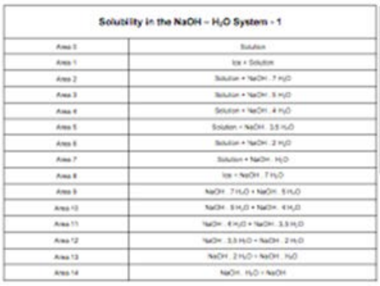
A2. Characteristics

Solubility

When an aqueous sodium hydroxide solution decreases and as soon as the freezing point is reached, the first crystal type is formed within the solution. With continuing cooling other crystal types are formed and the product starts to solidify. Preventing the solution from cooling will hinder crystallization. Diluting the solution will generally lower the temperature of solidification. Note that reducing the concentration from 45 w% to 40 w% NaOH in water actually increases the temperature of solidification, see Fig. A. 1

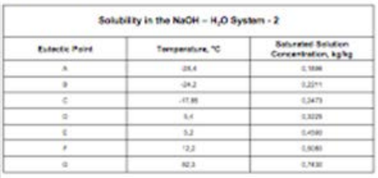
Fig. A. 1
Solubility diagram of aqueous NaOH in dependance of NaOH concentration in solution. [15]





Solubility in the NaOH – H_2O System - 1

Area 0	Solution
Area 1	Ice + Solution
Area 2	Solution + $NaOH \cdot 7\,H_2O$
Area 3	Solution + $NaOH \cdot 5\,H_2O$
Area 4	Solution + $NaOH \cdot 4\,H_2O$
Area 5	Solution + $NaOH \cdot 3{,}5\,H_2O$
Area 6	Solution + $NaOH \cdot 2\,H_2O$
Area 7	Solution + $NaOH \cdot H_2O$
Area 8	Ice + $NaOH \cdot 7\,H_2O$
Area 9	$NaOH \cdot 7\,H_2O$ + $NaOH \cdot 5\,H_2O$
Area 10	$NaOH \cdot 5\,H_2O$ + $NaOH \cdot 4\,H_2O$
Area 11	$NaOH \cdot 4\,H_2O$ + $NaOH \cdot 3{,}5\,H_2O$
Area 12	$NaOH \cdot 3{,}5\,H_2O$ + $NaOH \cdot 2\,H_2O$
Area 13	$NaOH \cdot 2\,H_2O$ + $NaOH \cdot H_2O$
Area 14	$NaOH \cdot H_2O$ + NaOH



Solubility in the NaOH – H_2O System - 2

Eutectic Point	Temperature, °C	Saturated Solution Concentration, kg/kg
A	-28,4	0,1896
B	-24,2	0,2211
C	-17,85	0,2473
D	5,4	0,3229
E	5,2	0,4580
F	12,2	0,5080
G	62,3	0,7430

Carbonation

Carbonation occurs when aqueous sodium hydroxide is exposed to air. Carbon dioxide (CO_2) present in the air is absorbed by aqueous NaOH and reacts with sodium carbonate (Na_2CO_3). If sodium carbonate is an important parameter for the end use, exposure to air should be minimized.

Shelf Life

Aqueous sodium hydroxide is an inorganic chemical. It has essentially an "infinite" shelf life and will remain intact until it is reacted with other chemicals. It is not subjected to any form of decomposition. Nevertheless, caution must be taken. Inside the storage tank, when aqueous sodium hydroxide is exposed to atmospheric carbon dioxide (CO_2), the sodium carbonate (Na_2CO_3) content will increase slowly. If the presence of sodium carbonate is critical to the application, the storage time should be limited or the product should be stored in a tank with a carbon dioxide free atmosphere. If aqueous NaOH is stored in a tank constructed of soft steel (1.0036 or similar), the iron (Fe) content will increase slowly. If the presence of iron is critical to the application, an alternative storage tank, constructed of a more appropriate material should be used. If liquid caustic soda is packed in a sealed container, the aging process of the packaging material it is in contact with, could affect shelf life. Depending upon the climate conditions and the product concentration, it may be necessary to insulate and/or install a heating system to the storage tanks.

Dilution

NaOH is highly hygroscopic. It readily dissolves in water causing an exothermic reaction. This affinity to water plays a major role in its application as an absorbent.

Neutralization

To neutralize sodium hydroxide, hydrochloric acid is used. Due to the highly exothermic reaction precaution must be taken to prevent splashes or exposure to fumes. To avoid an excessive temperature increase, dilute the concentrated solution before neutralization.

Reaction: $NaOH (l) + HCl (l) \rightarrow NaCl (l) + H2O (l)$

A3. Handling

Safety

It is important that those who handle caustic soda are aware of its highly reactive and corrosive properties and know what precautions to take. In case of accidental exposure, immediately flush exposed area with large amounts of water and seek medical attention. Appropriate protective equipment must be worn. This includes chemical splash goggles or face shield for eye and face protection, resistant rubber gloves, rubber boots and chemical suit.

Health Hazards

Sodium hydroxide is strongly corrosive and a powerful irritant by all routes of exposure (inhalation, ingestion, skin contact, and eye contact). It can cause severe burns and permanent damage to any tissue it contacts. The mechanism of burning is two-fold; thermal burns result from sodium hydroxide combining with moisture and consequent production of heat, and chemical burns result from reaction with organic molecules. Aerosols and airborne particles are very irritating to the upper respiratory tract and may cause pulmonary edema (accumulation of fluid in the lungs). Sodium hydroxide reacts quickly on contact with tissue and does not produce systemic toxicity (i.e., it does not produce effects distant from the point of contact).

Acute effects, resulting from short-term exposure to high concentrations of sodium hydroxide, include irritation and burning of the skin, eyes, nose, windpipe, and lungs. One-time, high-level inhalation of sodium hydroxide may lead to swelling of the larynx and irreversible obstructive lung disease. Early symptoms of ingestion include abdominal pain and vomiting. Perforation of the gastrointestinal tract and shock are also possible, and may not become apparent until several hours after ingestion. Contact with 25-50% solutions produces immediate skin irritation, while dilute solutions (4% or less) may not cause irritation for several hours. Eye contact initially causes burning and may lead to permanent eye damage.

Chronic effects resulting from long-term exposure to low concentrations of airborne sodium hydroxide include nose and throat irritation, chest pains, shortness of breath, and ulceration of the nasal passages.

Materials for handling aqueous sodium hydroxide

Sodium hydroxide is a corrosive chemical that is normally handled with steel, nickel, nickel alloys or certain types of plastic equipment. The specific material depends on the application. Factors such as temperature, solution concentration, location and safety standards all have to be considered. The most common construction materials for handling and storing NaOH are Steel in the range of material number 1.0036 to 1.0038. However high concentrated aqueous NaOH solutions will corrode these metals at elevated temperatures. Ideally aqueous NaOH solutions are stored at temperatures between 25 °C and 35 °C, preventing crystallization at low temperatures and corrosion at high temperatures. Where iron contamination or corrosion is unacceptable, epoxy lined steel and stainless steel with material number 1.4404 and 1.4301 are applicable. Stainless steels 1.4404 and 1.4301 are acceptable for temperatures up to 70 °C. At temperatures above this 2.4060 (nickel) or nickel coated steel is typically used. Other suitable alloys are material number 2.4360 (monel), 2.4816 (Inconel 600) or 2.4610 (Hastelloy C4). Plastics, such as polyethylene, polypropylene, PVC and CPVC are also chemically suitable with NaOH. They can be used to prevent iron contamination if maximum temperatures for each material are not exceeded. Aluminum, copper, zinc, lead and their alloys are not suitable. Aqueous NaOH readily attacks these materials. Heat exchangers are most commonly manufactured of stainless steel, whereby nickel, monel or inconel are preferred. At high temperatures stainless steel may crack.

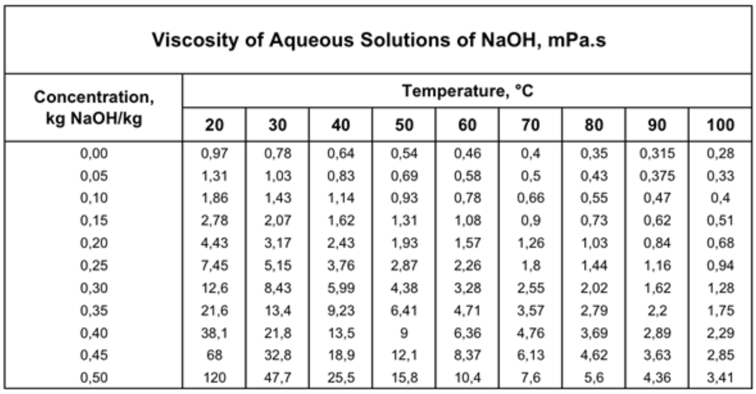
Storage Tank Design

Tanks that allow for minor corrosion and are kept at temperatures between 25 °C to 35 °C can be manufactured of steel material Nr. 1.0036 to 1.0038. In the design additional wall thickness for corrosion must be considered. If iron contamination is not allowed then stainless steel material Nr. 1.4404 or 1.4301 can be used. A more economical method can be to manufacture a steel vessel and include an epoxy coating on the inside. Plastic tanks are usually fabricated from polypropylene or fiber reinforced polymer and are suitable for temperatures up to 60 °C. In the fiber reinforced polymer vessels care must be taken to prevent NaOH contact with the fiber material to prevent corrosion. All tanks should be located within a diked area.

Piping

For the dimensioning of piping inner diameters the aqueous NaOH solution concentration must be taken into consideration. High concentrations have a high viscosity see Fig. A. 2. Proper pipeline design includes an adequate pitch to permit complete draining. Avoid any loops or pockets. This is especially important with high aqueous NaOH solutions due to the danger of crystallization at low temperatures. Adequate materials for piping as well as valves should be used in respect to corrosion and temperature. Plastic pipes e.g. GFRP with PP or PVC lining are adequate. Consideration must be given to the rapid pressure resistance decrease due to raise in temperature. Plastic pipes should be supported over their whole length.

Fig. A. 2
Viscosity of aqueous NaOH solutions in dependance of NaOH concentration in solution. (see yy)



Viscosity of Aqueous Solutions of NaOH, mPa.s

Concentration, kg NaOH/kg	Temperature, °C								
	20	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**
0,00	0,97	0,78	0,64	0,54	0,46	0,4	0,35	0,315	0,28
0,05	1,31	1,03	0,83	0,69	0,58	0,5	0,43	0,375	0,33
0,10	1,86	1,43	1,14	0,93	0,78	0,66	0,55	0,47	0,4
0,15	2,78	2,07	1,62	1,31	1,08	0,9	0,73	0,62	0,51
0,20	4,43	3,17	2,43	1,93	1,57	1,26	1,03	0,84	0,68
0,25	7,45	5,15	3,76	2,87	2,26	1,8	1,44	1,16	0,94
0,30	12,6	8,43	5,99	4,38	3,28	2,55	2,02	1,62	1,28
0,35	21,6	13,4	9,23	6,41	4,71	3,57	2,79	2,2	1,75
0,40	38,1	21,8	13,5	9	6,36	4,76	3,69	2,89	2,29
0,45	68	32,8	18,9	12,1	8,37	6,13	4,62	3,63	2,85
0,50	120	47,7	25,5	15,8	10,4	7,6	5,6	4,36	3,41

Valves

Stainless steel valves are recommended for aqueous sodium hydroxide applications.

Pumps

Centrifugal pumps of DIN Material Nr. 1.4404, 1.4301 or 2.4660 with either double mechanical seals or a deep packing gland are recommended. Packing material should be Polytetrafluoroethylene (PTFE) impregnated NaOH resistant fibers, or equivalent. To avoid sealing altogether, magnetically coupled pumps can be used. In addition issues with shaft tightening are avoided by using magnetic driven pumps.Membrane pumps are suitable for a consistent delivery dose of liquid caustic soda. The EPDM membrane should be provided with PTFE lining, and their housing should be made of PVC, PP or stainless steel. Pump location should receive careful consideration. For ease of operation, keep the suction lines as short as possible.

Gaskets

Gaskets made of modified PTFE or carbon with a nickel inlay should be used.

Meters

Aqueous NaOH solutions can be metered through standard rotameters having non-glass tubes and nickel or stainless steel floats. For strong, hot solutions magnetic, Coriolis or orifice type meters are preferred. A Coriolis flow meter applies the Coriolis-effect to measure mass flow rate and density of a fluid through a tube. The operating principle involves inducing a vibration of the tube through which the fluid passes. The vibration provides the rotating reference frame which gives rise to the Coriolis-effect.

Diluting a Solution

To dilute an aqueous NaOH solution the following equation can be applied:

$$D=V[A(B-C)/C]$$

Where: A = Specific gravity of strong solution B = Concentration of strong solution (w% NaOH) C = Concentration of weak solution (w% NaOH) D = Volume of water to be added V = Volume of strong solution

Note: When diluting aqueous NaOH by adding water, the volumes are not additive. The final volume does not equal volume of strong solution (V) plus volume of water (D). To calculate the final volume, the water and strong solution must be converted to a weight basis, and then divided by the density of the desired solution.

Appendix B Absorption Heat Pump

The absorption heat pump converts heat of a given temperature to heat of another temperature without any intermediate use of work compared to the vapor compression heat pump with its work input of compression [16].

The cycle employed in an absorption heat pump includes the following processes, whereby the absorbent is component A and the solvent (refrigerant) is component B of a mixture AB. Fig. B. 1 illustrates the heat pump process.

At point 1 component B is evaporated out of the solution AB by means of the driving heat Q2 (generator). Vapor B is then transferred at constant pressure p1 to the condenser. At point 2 vapor B is condensed at T1, releasing heat Q1". From point 2 to 3 the pressure is reduced by expansion to P0, and the liquid B is cooled to T0. At point 3 the liquid B is evaporated, absorbing the heat Q0 (evaporator). Vapor B is then transferred at constant pressure P0 to the absorber. At point 4 vapor B is absorbed by forming solution AB and rejecting the heat Q1 at T1 (absorber). In addition at point 4 the pressure of the solution AB is increased from P0 to P1 due to the raise in temperature, and AB is transferred from the absorber to the generator. Simultaneously, fresh absorbent is transferred from the generator to the absorber.

For processes 1 and 3, heat is supplied to the cycle and for processes 2 and 4 heat is rejected.

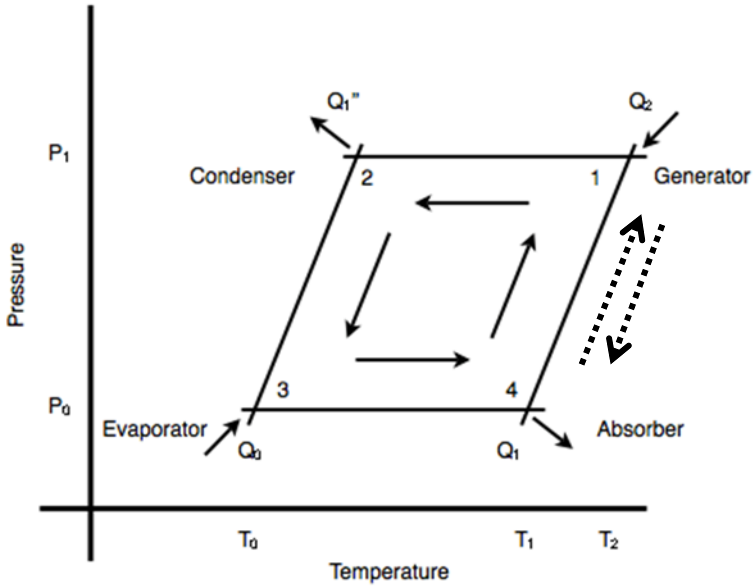
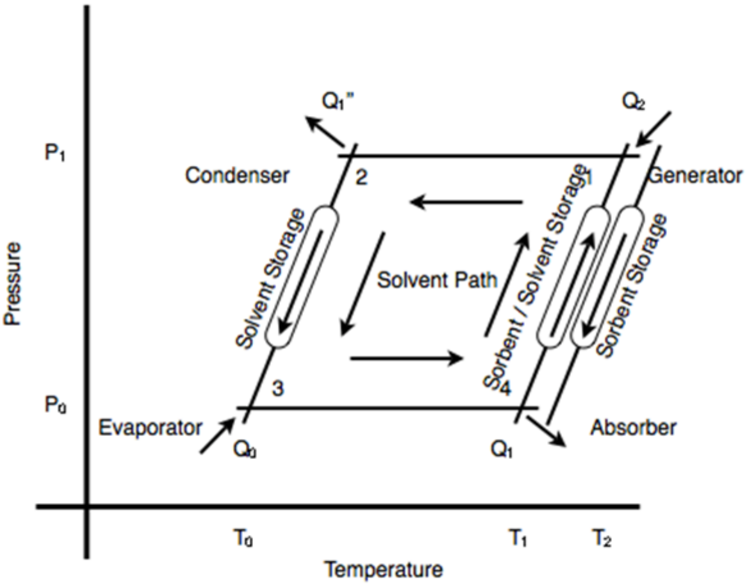


Fig. B. 1
Processes in an absorption heat pump. The arrows inside the rhombus depict the circulation of solvent B. The arrows on the right side (dotted) show the circulation from absorbent A.

In the case of a thermal storage system based on the absorption heat pump principle, the absorption cycle is interrupted. Instead of allowing component B to move directly from condenser to evaporator, it is stored. In the same manor component A is stored rather then transferred from generator to absorber (Fig. B. 2). In charging only process 1 and 2, generator and condenser are operated. In the discharging mode stored components A and B are transferred from the store to the absorber and evaporator, closing the loop. Component B is evaporated using Q0 and absorbed by component A on the absorber, releasing Q1. The solution AB is then stored for recharging.

Fig. B. 2
Processes in a thermal storage based on the absorption heat pump principle.



Due to the interruption in the absorption cycle, generator and absorber, as well as condenser and evaporator can be unified to make one component each.

Appendix C MATLAB Simulation Model

Simulation Tool

MATLAB is a multi-paradigm numerical computing environment and programming language, developed by MathWorks. MATLAB allows matrix manipulations, plotting of functions and data, implementation of algorithms, creation of user interfaces, and interfacing with programs written in other languages like C and FORTRAN. The additional package Simulink, allows for graphical simulation and model-based design for dynamic and embedded systems.

Simulation structure

The Matlab simulation model as represented in Fig. C. 1 was designed and comprises:

1. A detailed model of a plate collector to charge the storage (module 1)
2. The actual storage model including various system components (modules 2+3)
3. A building model representing the loads for heating or DHW production (module 4)

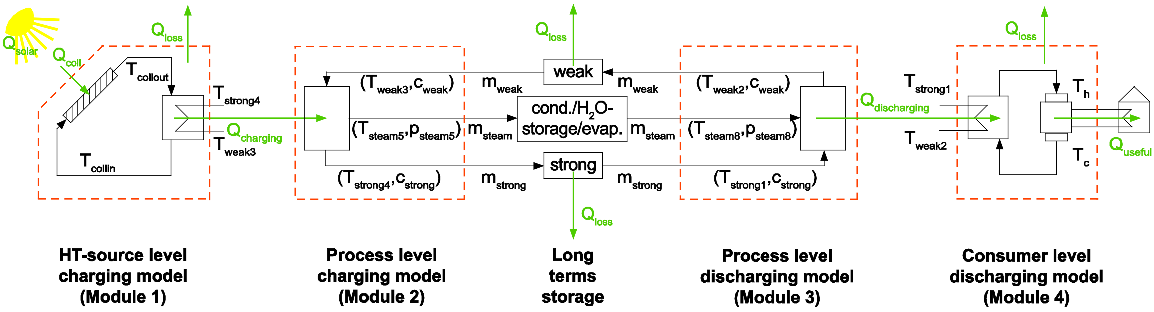
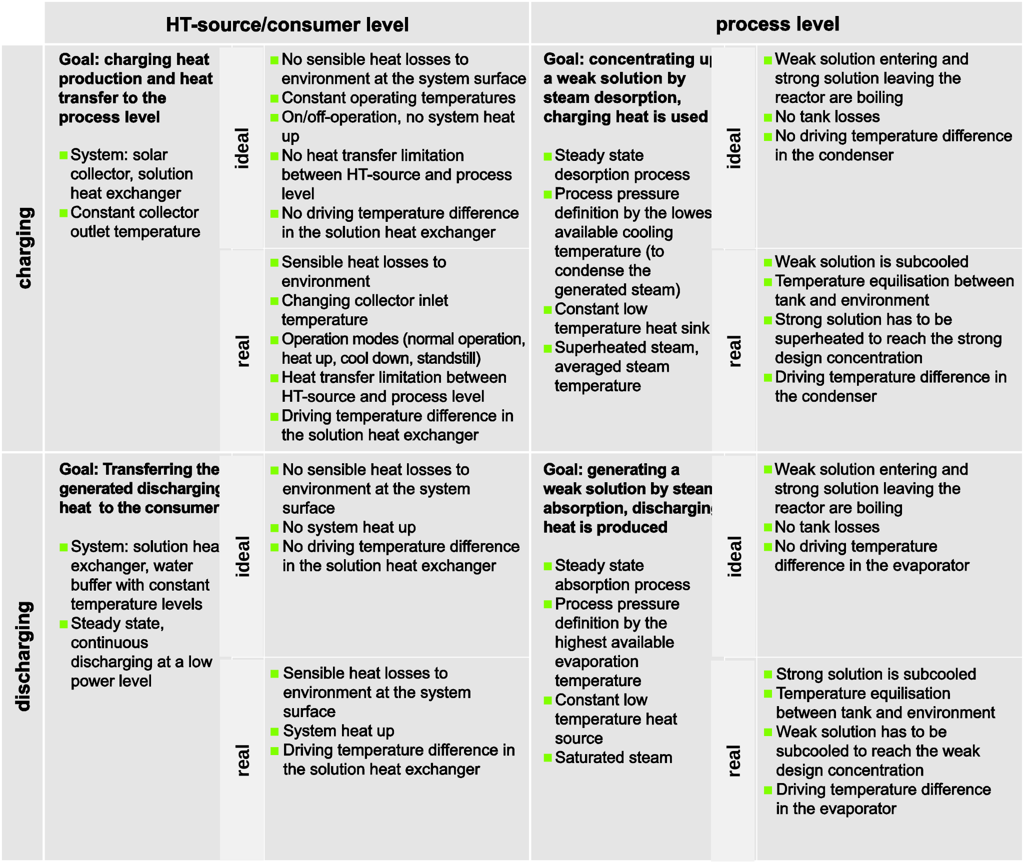


Fig. C. 1 Overall system model, schematic

The Simulation followed two pathways as depicted in Fig. C. 2:

1. Simulation of an optimal behavior of the whole storage system including building loads
2. Simulation of a ”real” behavior of the whole storage system including building loads. This means that heat losses are included and additional temperature losses in heat exchangers are added



	HT-source/consumer level			process level		
charging	**Goal: charging heat production and heat transfer to the process level** ■ System: solar collector, solution heat exchanger ■ Constant collector outlet temperature	ideal	■ No sensible heat losses to environment at the system surface ■ Constant operating temperatures ■ On/off-operation, no system heat up ■ No heat transfer limitation between HT-source and process level ■ No driving temperature difference in the solution heat exchanger	**Goal: concentrating u a weak solution by steam desorption, charging heat is used** ■ Steady state desorption process ■ Process pressure definition by the lowes available cooling temperature (to condense the generated steam) ■ Constant low temperature heat sink ■ Superheated steam, averaged steam temperature	ideal	■ Weak solution entering and strong solution leaving the reactor are boiling ■ No tank losses ■ No driving temperature difference in the condenser
		real	■ Sensible heat losses to environment ■ Changing collector inlet temperature ■ Operation modes (normal operation, heat up, cool down, standstill) ■ Heat transfer limitation between HT-source and process level ■ Driving temperature difference in the solution heat exchanger		real	■ Weak solution is subcooled ■ Temperature equilisation between tank and environment ■ Strong solution has to be superheated to reach the strong design concentration ■ Driving temperature difference in the condenser
discharging	**Goal: Transferring the generated discharging heat to the consumer** ■ System: solution hea exchanger, water buffer with constant temperature levels ■ Steady state, continuous discharging at a low power level	ideal	■ No sensible heat losses to environment at the system surface ■ No system heat up ■ No driving temperature difference in the solution heat exchanger	**Goal: generating a weak solution by stean absorption, dischargin heat is produced** ■ Steady state absorption process ■ Process pressure definition by the highest available evaporation temperature ■ Constant low temperature heat source ■ Saturated steam	ideal	■ Weak solution entering and strong solution leaving the reactor are boiling ■ No tank losses ■ No driving temperature difference in the evaporator
		real	■ Sensible heat losses to environment at the system surface ■ System heat up ■ Driving temperature difference in the solution heat exchanger		real	■ Strong solution is subcooled ■ Temperature equilisation between tank and environment ■ Weak solution has to be subcooled to reach the weak design concentration ■ Driving temperature difference in the evaporator

Fig. C. 2 Assumptions for the ideal and the real case.

Matlab has graphical programming capabilities that were used in this project for state definition. Fig. C. 3 shows as an example the state diagram for “HT- source level charging”. 16 of these states were programmed to cover all possible In- and Output cases. All those cases where again programmed for the “ideal” and the “real” case.

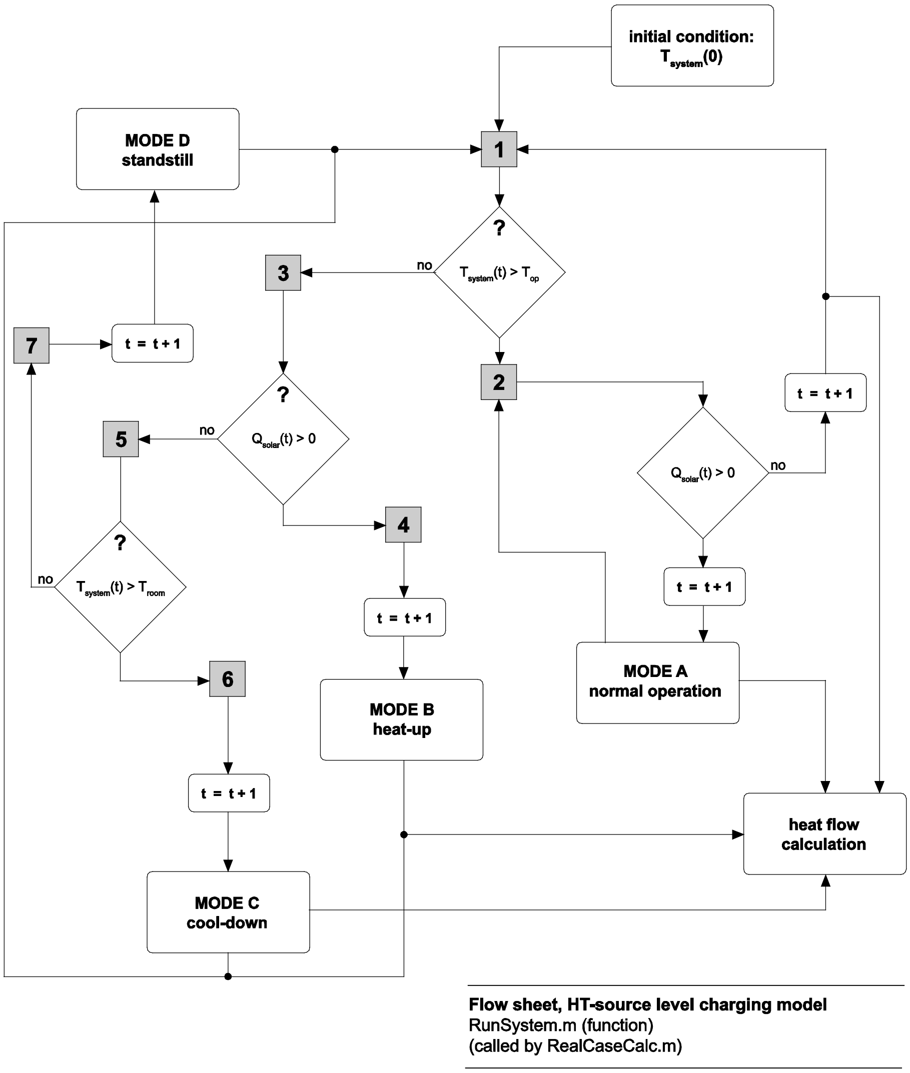
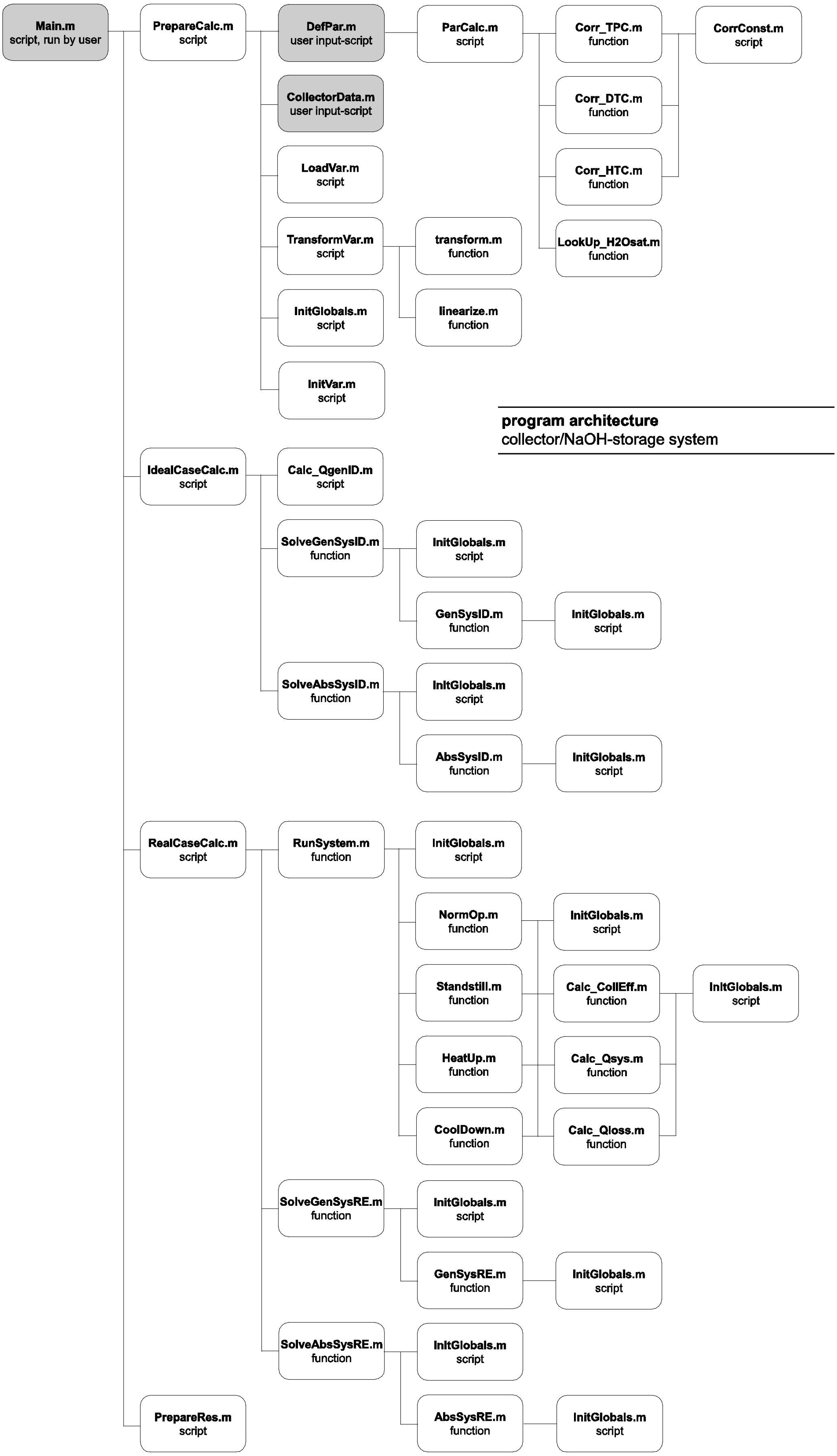


Fig. C. 3 Flow diagram which show the HT-source level charging

In Fig. C. 4, the over-all architecture of the MATLAB simulation model is shown, including all individual scripts (m-files) that were necessary for the representation of the real plant within this simulation framework.

Fig. C. 4 Program architecture in Matlab



Appendix D TRNSYS Simulation Model

Nomenclature

Abbreviations

GHX	Ground Heat Exchanger
SC	Solar Collector
LC	Low Concentration sorbent / solvent solution
MC	Middle Concentration sorbent / solvent solution
HC	High Concentration sorbent / solvent solution
TL	Thermal Load (domestic hot water or space heating)
calc.	Calculate
inc.	Increase
HE	Heat Exchanger
Ge	Generator
Ab	Absorber
Co	Condenser
Ev	Evaporator
Su	Solution
Sv	Solvent
BC	Bypass circulation
STS	Sensible Thermal Storage
SH	Space Heating
DHW	Domestic Hot Water
FS	First Stage
SS	Second Stage

Symbols

c [$J \cdot g^{-1} \cdot K^{-1}$]	Specific heat capacity
C [J·K-1]	Heat capacity
λ [$W \cdot m^{-1} \cdot K^{-1}$]	Thermal conductivity
Nu	Nusselt number
T [K]	Temperature
$\dot{m}$ [$kg \cdot s^{-1}$]	Mass flow rate
ω [$m^3 \cdot m^{-3}$]	Volume Concentration
U [$W \cdot m^{-2} \cdot K^{-1}$]	Heat transfer coefficient
A [m^2]	Area
H [J]	Enthalpy
h [$J \cdot kg^{-1}$]	Specific enthalpy
m [kg]	Mass

Simulation Tool

For the simulations the TRNSYS Program was used. TRNSYS is a transient system simulation program with a modular structure. It recognizes a system description language in which the user specifies the components that constitute the system and the manner in which they are connected. The TRNSYS library includes many of the components commonly found in thermal and electrical energy systems, as well as component routines to handle input of weather data or other time dependent forcing functions and output of simulation results. The modular nature of TRNSYS gives the program flexibility, and facilitates the addition to the program of mathematical models not included in the standard library. The program facilitates a graphical interface.

Simulation Structure

The NaOH simulation model was built on the following major components from the standard library:

- Solar collector
- Sensible thermal storage
- Heat exchanger
- Building (thermal behavior)
- Ground heat exchanger

To structure the charging process during the runtime of the simulation the loads were given the following priorities (see Fig. D. 1):

1. Priority: Sensible thermal storage
2. Priority: Building
3. Priority: NaOH Storage

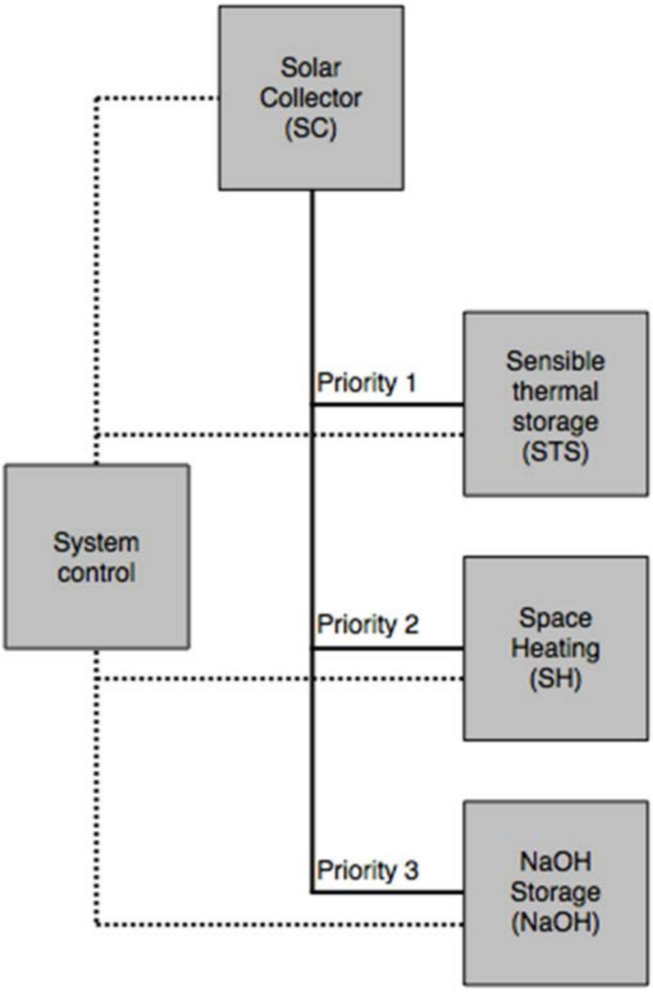
An overlaid controller regulates the charging and discharging in respect to the priorities and thermal state of the components, as well as regulating the source of heat for the buffer, wether from the solar collectors or the NaOH storage.

If the solar irradiation is below 200 $W\cdot m^{-2}$ the mass flow from the solar collectors is set to zero and no solar thermal power is supplied.

NaOH module

The NaOH storage is a chemically driven heat pump, charged using solar thermal energy. The enthalpy released in discharging is gained from a ground heat exchanger. The main components of the NaOH storage are heat / mass exchangers. In the simulation program the heat / mass exchanger temperature is calculated using the logarithmic mean temperature difference (ΔT_{lm}) and the sorbent / solvent solution quantities and concentrations are derived from the law of conservation of mass and energy. To calculate the involved substance properties, relations between temperature, vapor pressure and concentrations of the solutions are established.

Fig. D. 1
Diagram of the Simulation including source and the storage with varying priority.



Model Equations

The NaOH storage simulation is bases on the following equations:

Conservation of mass:

$$m_1 = m_2 + m_3$$

$$m_{Su,LC} = m_{Su,MC} + m_{Sv}$$

$$m_1 \cdot \omega_1 = m_2 \cdot \omega_2$$

$$m_{Su,LC} \cdot \omega_{Su,LC} = m_{Su,MC} \cdot \omega_{Su,MC}$$

Conservation of energy:

$$H_1 = H_2 + H_3$$

$$H + m_1 \cdot h_1 = m_2 \cdot h_2 + m_3 \cdot h_3$$

$$H_{Ge} + m_{Su,LC} \cdot h_{S,LC} = m_{Su,MC} \cdot h_{Su,MC} + m_{Sv} \cdot h_{Sv}$$

Logarithmic mean temperature difference:

$$\Delta T_{lm} = \Delta T_2 - \Delta T_1 / \ln(\Delta T_2 / \Delta T_1)$$

The non-linear properties of the aqueous hydroxide sorbent / solvent solutions are gained from functions acquired from ASHRAE [17] for pure solvent and from a paper by Olsson [11].

The heat / mass exchangers are considered to be counter-flow. Assuming that there are no energy losses the following heat capacity equation is valid:

$$C_{HE} = (\dot{m}_1 \cdot c_1 \cdot (T_{out} - T_{in}))_{COLD} = (\dot{m}_2 \cdot c_2 \cdot (T_{in} - T_{out}))_{HOT}$$

Furthermore the thermal energy can be expressed as:

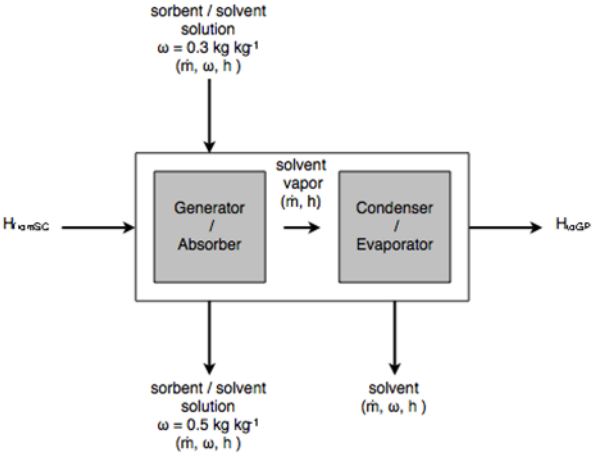
$$H = U \cdot A \cdot \Delta T_{lm}$$

D2. Energy flow in Charging and Discharging

Charging single stage

In the sing stage charging process (Fig. D. 2), solar thermal energy H_{fromSC} and sorbent / solvent solution of a concentration of $\omega = 0.3\,kg{\cdot}kg^{-1}$ are introduced to the generator. The resulting solvent vapor is transported from generator to condenser where it is condensed, releasing the enthalpy to the ground heat exchanger. The resulting sorbent / solvent solution of $\omega = 0.5\,kg{\cdot}kg^{-1}$ and solvent are collected and stored.

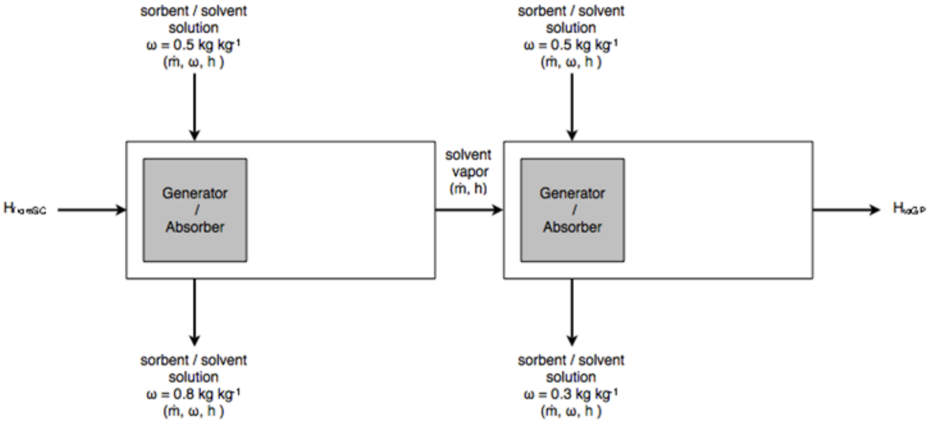
Fig. D. 2
Schema of the single stage charging process.



Charging double stage

The double stage charging process (Fig. D. 3) includes the single stage process as a first stage, achieving a sorbent / solvent solution concentration of $\omega = 0.5\,kg{\cdot}kg^{-1}$. A second stage is introduced to increase the concentration to $\omega = 0.8\,kg{\cdot}kg^{-1}$. To reach this the $\omega = 0.5\,kg{\cdot}kg^{-1}$ solution is introduced to both generator / absorber heat / mass exchangers. The first exchanger is heated from a solar source and the second generator is cooled from the ground heat exchanger. In this manner sorbent is once again evaporated on the heated generator and condensed on the cooled one. The results are a high concentration of $\omega = 0.8\,kg{\cdot}kg^{-1}$ and a low concentration of $\omega = 0.3\,kg{\cdot}kg^{-1}$. This is favorable due to the higher temperatures T_{toTL} reached with higher concentrations.

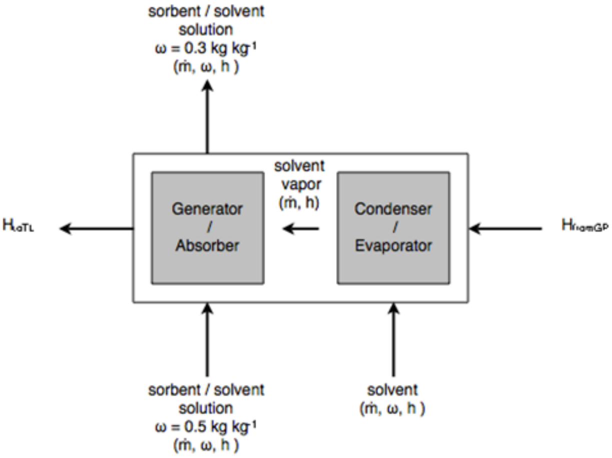
Fig. D. 3
Schema of the double stage charging process.



Discharging single stage

For discharging single stage (Fig. D. 4), solvent is introduced to the condenser / evaporator heat / mass exchanger and evaporated by low temperature enthalpy from the ground heat exchanger. The solvent vapor is condensed on the generator / absorber heat / mass exchanger by introducing concentrated sorbent / solvent solution. In this process of condensing the enthalpy of evaporation is released to the solution, functioning as a chemical heat pump.

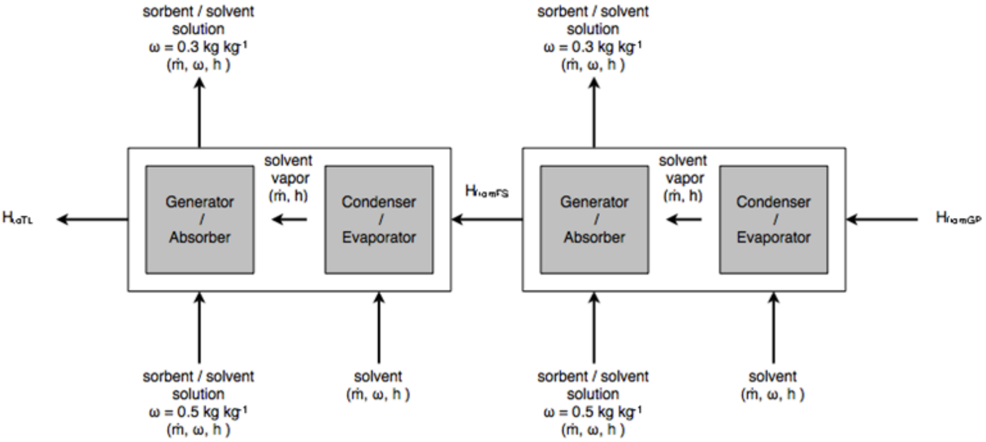
Fig. D. 4
Schema of the single stage discharging process.



Discharging double stage

The double stage charging process (Fig. D. 5) includes the single stage process as a first stage, achieving a rise in temperature ΔT_{FS} of approximately 30 K from $T_{fromGHX} = 10$ °C to $T_{fromFS} = 40$ °C. The enthalpy H_{fromFS} is then introduced to the second stage condenser / evaporator heat / mass exchanger in place of $H_{fromGHX}$. The second stage functions identical to the first stage apart from the input temperature being approximately 40 °C and not as in the first stage approximately 10 °C. In this process higher temperatures required for DHW can be reached.

Fig. D. 5
Schema of the double stage charging process.



Program Structure

The NaOH storage program is divided into three modules, consisting of a main module and two submodules. The program is structured as follows:

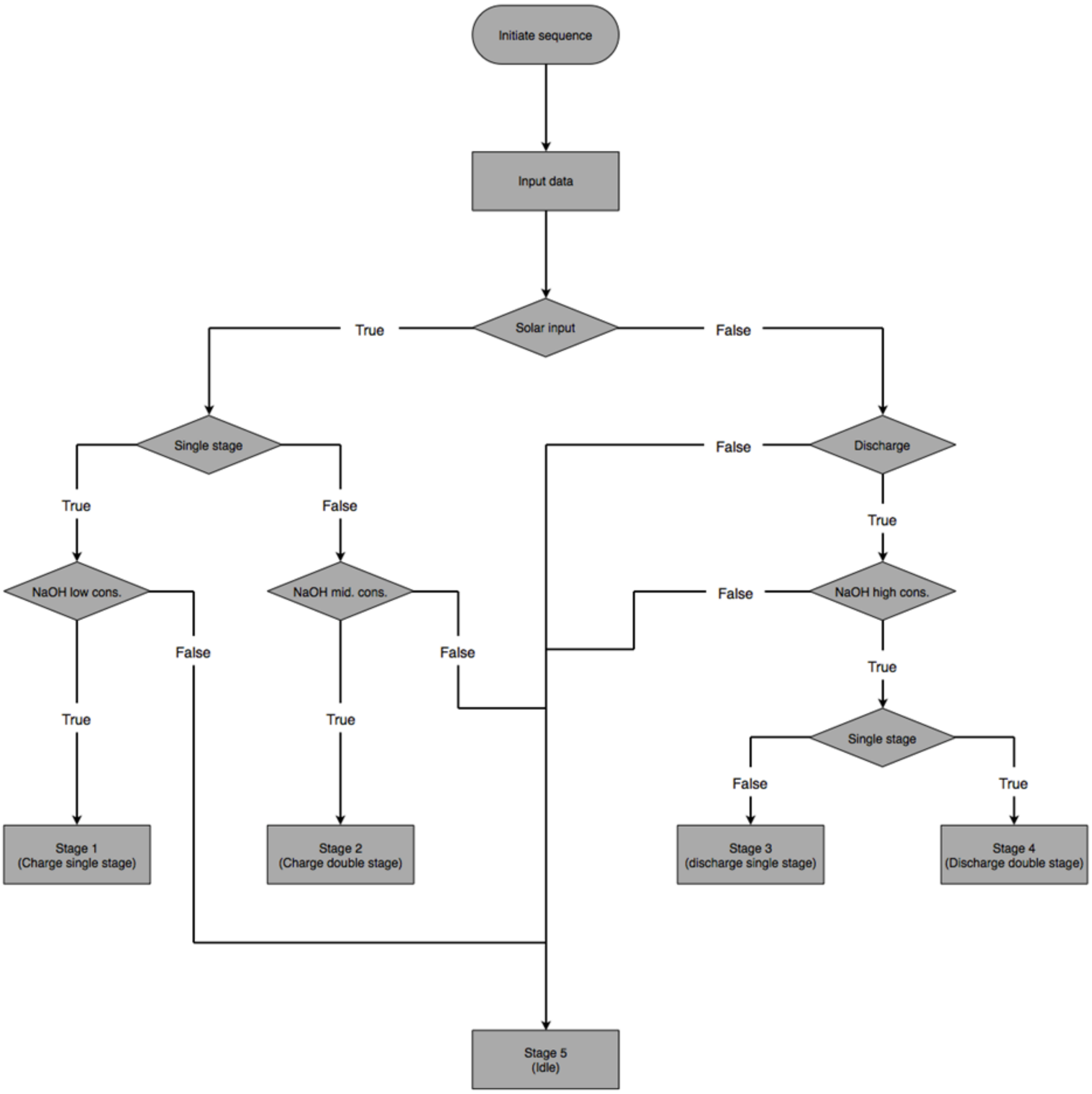
- read input parameters
- chose charging / discharging process
- update storage state

In hourly intervals the main module determines the operating mode and initiates one of the two submodules. The input readings consist of the values from the:

- Solar collector (SC)
- Ground Heat Exchanger (GHX)
- NaOH storage vessels
- Space heating (SH)
- Domestic hot water (DHW)

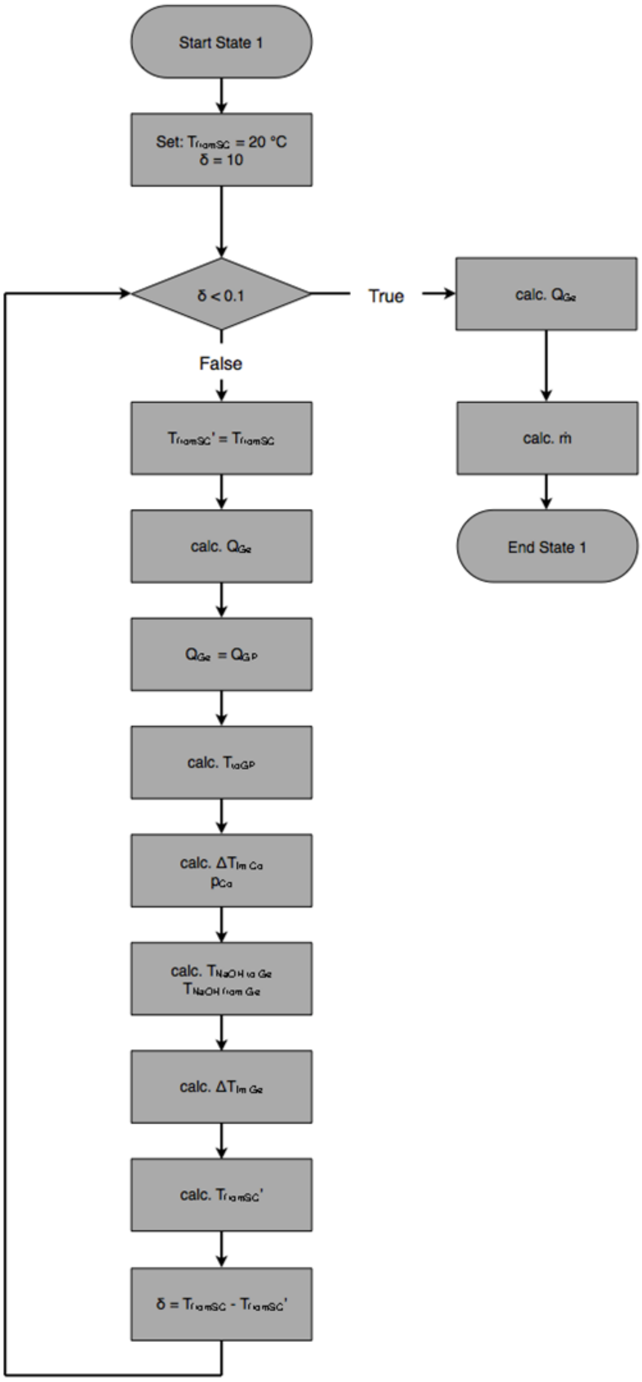
Main module process flow diagram

The solar input determines if the charging submodule is chosen whereby the discharging submodule is dependent on the discharge mass flow. In both modules, dependent on the temperature state or requirement, the single or double stage is chosen. For all other conditions the idle mode 5 is chosen.



Charging Submodule

The charging submodule is chosen if there is a mass flow ($\dot{m}$) from the solar collector (SC). Nevertheless an effective charging process is not guaranteed, this is dependent on the thermal energy supplied (HSC = $\dot{m}_{SC} \cdot T_{SC}$).



Initially a fixed value $T_{fromSC} = 20$ °C is set as well as $\delta = 10$ to guaranty at least one iteration through the submodule. Once the condition $\delta < 0.1$ is fulfilled, the generator thermal energy (H_{Ge}) is calculated from which the mass flows, $\dot{m}_{Su,HC}$, $\dot{m}_{Su,MC}$, $\dot{m}_{Su,LC}$ and $\dot{m}_{Sv}$ are derived.

The solar energy input is:

$$H_{SC} = \dot{m}_{SC} \cdot c_{SC} \left(T_{fromSC} - T_{toSC}\right)$$

System losses are 10 % of the energy flow:

$$H_{Ge} = 0.9\, H_{SC}$$

It is assumed that the energy released to the ground heat exchanger equals the generator energy:

$$H_{toGHX} = H_{Ge}$$

This condition is met when all solvent vapor is condensed, releasing the latent energy to the ground heat exchanger, the pressure in the generator / absorber and condenser / evaporator is constant and no thermal energy is released to the atmosphere.

By calculating the logarithmic temperature difference (ΔT_{lm}) of the condenser, it is possible to define the mean temperature of the solvent.

$$\Delta T_{lm,Co} = T_{toGHX} - T_{fromGHX} / \ln((T_{toGHX} - T_{Sv}) / (T_{fromGHX} - T_{Sv})$$

This in turn allows the pressure in the generator / absorber and condenser / evaporator to be defined using the information from ASHRAE and Olsson.

With the pressure and the sorbent / solvent solution concentration defined, it is now possible to calculate the solution temperature on the generator (T_{So}):

$$\ln(p_{Co}) = a + (b / (c + \Delta T_{So}))$$

a, b, and c are solution specific constants.

Once all the temperatures inside the NaOH system are calculated the new solar temperature T_{fromSC} is calculated

The mass flows of the aqueous NaOH solutions and the reaction water are calculated from the enthalpy value and applying the laws of conservation of mass and energy.